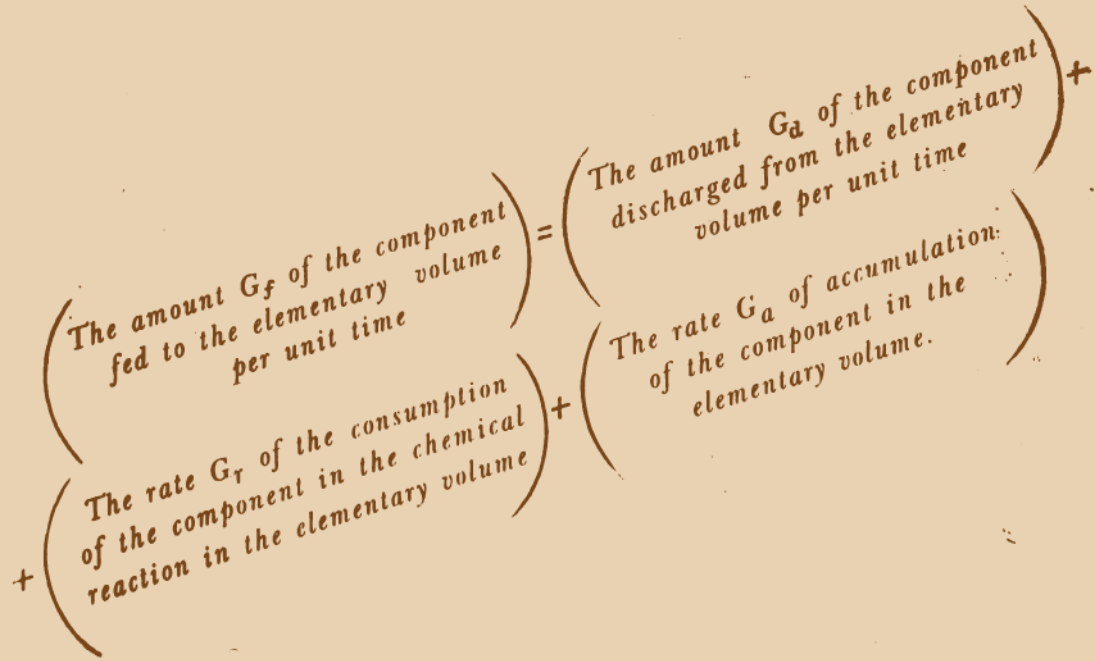
Calculations of Chemical Technological Processes

Edited by
I. P. Mukhlyonov, D.Sc.


The amount G_f of the component fed to the elementary volume per unit time
=
The amount G_d of the component discharged from the elementary volume per unit time
+
The rate G_r of the consumption of the component in the chemical reaction in the elementary volume
+
The rate G_a of accumulation of the component in the elementary volume.

Mir Publishers

The authors wrote this workbook as a complementary volume to their popular textbook **Chemical Technology** (Mir Publishers, 1979).

The problems discussed in the book cover a wide range of the basic processes of chemical technology. A special attention is paid to calculation techniques and procedures, particularly, for process kinetics and reactor designs of various types. The book is intended for undergraduates specializing in chemical technology.

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'CAL TECHNOLOGY, Vols. I-II

ILYONOV, D.Sc. (Editor)

. textbook is intended for chemical engineering students. Scientists and engineers working in the field of chemical engineering will find the book quite useful.

The first volume contains generalization and description of the theoretical foundations of chemical engineering applicable to homogeneous, heterogeneous and catalytic processes. Special attention has been paid in this volume to a study of macrokinetics of chemical processes and theory of chemical reactors. New material, formulas and tables necessary for calculations of chemical processes and reactors, and basic information about raw materials have been included.

The second volume deals with the application of basic laws for determining optimal parameters and selection of reactors for chemical engineering processes of utmost national economic importance. It cites as examples the processes for production of sulphuric acid, ammonia, nitric acid, mineral salts and fertilizers, silicates, metallurgical and electrochemical products, as well as processes for rendering industrial waste harmless.

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РАСЧЕТЫ ХИМИКО-ТЕХНОЛОГИЧЕСКИХ ПРОЦЕССОВ

Под общей редакцией
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Calculations of Chemical Technological Processes

Edited by
I. P. Mukhlyonov

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Preface

The future chemical engineers should have a good understanding of the scientific fundamentals and typical features of the chemical technological processes and the interrelationships between these processes to be able to control integrated production processes, to develop such processes, and to carry out research work at the time when chemical technology undergoes further specialization and differentiation. The university students are given such knowledge in the "General Chemical Technology" course.

The lecture course is accompanied by practical studies in which students make calculations of the chemical technological processes. At first students get acquainted with the fundamental equations and then proceed to making calculations for specific technological processes determining the rates of the chemical processes taking into account the relationship between the rates of the diffusion processes and chemical reactions and their dependence on the technological parameters. The studies give the students the skills for application of the equations corresponding to the mathematical models of the reaction vessels and for wide use of diagrams and nomograms.

This book has been written according to the standard programme of the "General Chemical Technology" course for universities. The contents of the book include the principles for drawing up the material and heat balances, calculations of equilibrium and kinetics of the homogeneous and heterogeneous (mass-exchange) processes, calculations of electrochemical production processes and chemical reaction vessels, etc. Each section of the book includes typical examples and problems to be solved by the students. The material of the book is based on the actual industrial and design data provided by various chemical plants and design institutions in the USSR. Some material has been taken from such well-known manuals as "Calculations in Technology of Inorganic Compounds" by M. E. Pozin et al., "Chemical Engineering Calculations" by S. D. Beskov, "Chemical Reaction Engineering" by O. Levenspiel, "Reaction Kinetics for Chemical Engineers" by S. Walas, and others. In each case this is specially noted in the text.

For the most part the material of the book has been used by the authors in teaching and in laboratory excercises for the students. Some material has been included in the term and diploma papers prepared by the students.

All the material and heat balances in the book are calculated for the standard conditions—the pressure of 1.01325×10^5 Pa and the temperature of 0°C.

The book was written by the faculty members of the Leningrad Technology Institute from the Chair of Basic Chemical Technology and the Chair of the Chemical Process Models. Chapters I and II were written by E. S. Rumyantseva, Chapter III by A. Ya. Averbukh, Chapters IV, V, and VIII by A. F. Tubolkin, Chapter VI by E. S. Tumarkina, and Chapter VII by E. Ya. Tarat and V. A. Kholodnov. The introductions to all chapters were written by I. P. Mukhlyonov in collaboration with the authors of the respective chapters.

The authors are grateful to T. P. Bondarchuk, A. T. Bartov, V. M. Pomerantsev, A. N. Prokopenko, A. G. Antonenkov, and A. A. Moskvin for the valuable advice and suggestions.

The authors would welcome any comments and proposals from the readers.

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Part One

Material and Heat Calculations of the Chemical Technological Processes

Chapter I

The Basic Principles for Drawing up Material Balances and Material Calculations for Irreversible Chemical Technological Processes

Introduction

The chemical technological calculations are the main and the most labour-consuming component of the design for any chemical industrial process. Such calculations are also made in conclusion of technological studies in laboratories and in surveys of operating plants and production lines. The calculations may be done to determine kinetic constants and optimum parameters of a chemical process or to find the reaction volumes and the main sizes of reaction vessels.

The technological calculations are based on the material and heat calculations. The material calculations are made to determine the yields of the main and secondary products, consumption coefficients for the raw materials and the production losses. Only when the material flows are known can the engineer make calculations required for designing the production equipment and service connections and estimate the cost efficiency and usefullness of the process. Be it planning of a new production process or analysis of operation of an existing process, the engineer always has to draw up the material balance. The planners of new production processes take into account the experience accumulated with the available processes and make use of the advanced research results. The comparative technical and economical analysis of the available processes makes it possible to select the most efficient technology and the optimum plant design and conditions of the process.

The material balance can be written down as an equation the left-hand side of which is the sum of the masses $\sum G$ of all the input

materials and the right-hand side is the sum of the masses $\sum G'$ of the products and the production losses G'_{loss}:

$$\sum G = \sum G' + G_{loss} \qquad (I.1)$$

The material balance is based on conservation of mass and the stoichiometric relationships.

The material balance is drawn up according to the equation of the main overall reaction taking into account the secondary reactions on the basis of the mass conservation law. The total mass of all the materials coming into the apparatus (plant), that is, the input, is equal to the total mass of the products going out, that is, the output. The material balance can be worked out per unit mass (kg, ton) of the main product or per unit time (hour, day). The masses of the inputs and outputs are determined separately for the solid, liquid and gaseous phases according to the following equation:

$$G_s + G_l + G_g = G'_s + G'_l + G'_g \qquad (I.2)$$

A process does not always involve all phases or one phase can consist of several materials so that Eq. (I.2) can be written in a simpler or more complicated form.

When the total balance is drawn up this typically involves solving a system of equations (I.1) with several unknowns. There can also be used the equations for determining the equilibrium and actual yields of the products, the rate of the process, and so on.

The *theoretical* material balance is calculated from the stoichiometric equation of the reaction. Only the knowledge of the reaction equation and the molecular masses of the components is needed to draw up this balance.

The *practical* material balance takes into account the compositions of the starting material and the final products, the excess of any of the components, the degree of transformation, the losses of the raw materials and the final products, etc.

The material balance can be used to find the consumption of raw materials and additives for a given output of the apparatus or plant, the production unit costs, the yields of the products, the capacity of the reaction zone, the numbers of reaction vessels and the production losses (unproductive consumption of the raw materials and products owing to leaks, spilling or entrainment).

Proceeding from the material balance the heat balance is drawn up which shows the demands for fuel, the capacity of the heat-exchange surfaces and the consumption of heat or cooling agents. All these data can be summarized in a table (see Table 1).

Calculations are usually made in mass units (kg, ton) or in moles. The balance in volume units (cubic metres) can be drawn up only for some gas-phase reactions without volume changes.

TABLE 1

Material Balance

(G_1, G_2 and G_3 are the masses of the starting reactants and G_4, G_5, and G_6 are the masses of the main product, by-products, and the waste products, respectively.)

INPUTS				OUTPUTS			
Materials	kg	m^3	%	Products	kg	m^3	%
G_1				G_4			
G_2				G_5			
G_3				G_6			
Total:				*Total*:			

The *consumption coefficients* describe consumption of various types of raw materials, water, fuel, electric power, and steam per unit product. The plant design and technological process parameters should provide for the optimum combination of a high intensity and productivity of the process and a high quality of the products and the lowest possible production unit costs.

The production costs include the expenditures for production and marketing of the products. To calculate the production unit costs the engineer uses the consumption coefficients for raw and other materials, fuels and energy and their current prices. The lower are the consumption coefficients the more economical is the process and the lower is the unit cost of the product. However, reduction of the consumption coefficients below a certain level can necessitate increasing the purity of the starting materials, the recovery rates and the yields of the products so that the resulting investments can increase the production unit costs.

Of especial importance are the consumption coefficients for raw materials since their costs account for the 60-70% of the production costs in most chemical processes.

To determine the consumption coefficients the engineer should have knowledge of all the stages of the technological process by which the starting material is transformed into the end product.

The theoretical consumption coefficients A_{th} are based on the stoichiometric relationships describing the transformation of the starting material into the end product. The practical consumption coefficients A_{pr} also take into account the production losses at all the stages of the process and the side reactions if they occur.

The consumption coefficients for the same product can vary depending on the composition of the starting material, and the difference can be considerable. Therefore, when the raw materials have to

be transported some distance to the production plant the planners should first estimate the consumption coefficients for various types of the raw materials to select the most economical option.

Calculations of Consumption Coefficients

Problem 1. Determine the theoretical consumption coefficients for the following iron ores used in production of pig iron containing 92% Fe assuming that the ores do not contain impurities and dirt.

	M
Spathic iron ore $FeCO_3$	115.8
Limonite $2Fe_2O_3 \cdot 3H_2O$	373
Goethite $2Fe_2O_3 \cdot 2H_2O$	355
Specular iron ore Fe_2O_3	159.7
Magnetic iron ore Fe_3O_4	231.5

Here M is the molecular mass.

Solution. $FeCO_3$: 1 kmole of $FeCO_3$ yields 1 kmole of Fe or 115.8 kg of $FeCO_3$ give 55.9 kg of Fe. Hence, to produce 1 ton of pig iron with 92% Fe content we need

$$\frac{1 \times 0.92 \times 115.8}{55.9} = 1.9 \text{ tons of } FeCO_3$$

In a similar way we can find the theoretical consumption coefficients for other iron ores.

$2Fe_2O_3 \cdot 3H_2O$:

$$\frac{1 \times 0.92 \times 373}{4 \times 55.9} = 1.55 \text{ tons}$$

$2Fe_2O_3 \cdot 2H_2O$:

$$\frac{1 \times 0.92 \times 355}{4 \times 55.9} = 1.45 \text{ tons}$$

Fe_2O_3:

$$\frac{1 \times 0.92 \times 159.7}{2 \times 55.9} = 1.33 \text{ tons}$$

Fe_3O_4:

$$\frac{1 \times 0.92 \times 231.5}{3 \times 55.9} = 1.28 \text{ tons}$$

Problem 2. Calculate consumption of the alunite ore containing 23% Al_2O_3 for production of 1 ton of aluminium if the losses of aluminium at the production stages amount to 12% (by mass).

The formula of alunite can be written as $3Al_2O_3 \cdot K_2O \cdot 4SO_3 \cdot 6H_2O$, the molecular mass of alunite is 828.

Solution. The process for producing metallic aluminium from alunite consists of two stages:

1. Production of alumina (aluminium oxide) by roasting the alunite ore at 500-580 °C and treating it with ammonia solution. The precipitate of Al_2O_3 and $Al(OH)_3$ is treated with 10-12% solution of NaOH producing the aluminate solution which is treated with CO_2 and gives the precipitate of $Al(OH)_3$. Alumina is produced by roasting the precipitate.

2. The metallic aluminium is produced by electrolysis of aluminium oxide dissolved in molten cryolite Na_3AlF_6.

Production of 1000 kg of aluminium theoretically requires

$$\frac{102 \times 1000}{2 \times 27} = 1900 \text{ kg of } Al_2O_3$$

Here 102 is the molecular mass of Al_2O_3 and 27 is the molecular mass of aluminium. The amount of pure alunite required for production of 1 ton of aluminium is

$$\frac{1900 \times 828}{3 \times 102} = 5100 \text{ kg}$$

The content of Al_2O_3 in alunite is

$$\frac{3 \times 102 \times 100}{828} = 37\%$$

The alunite ore in this problem contains 23% Al_2O_3. Hence, to produce 1 ton of aluminium we need the following amount of the alunite ore of the specified composition assuming full utilization of the ore:

$$\frac{5100 \times 37}{23} = 8200 \text{ kg} = 8.2 \text{ tons}$$

The practical consumption coefficient taking into account the production losses at all the stages of production is

$$A_{pr} = \frac{8.2}{0.88} = 9.35 \text{ tons}$$

Problem 3. Calculate consumption of benzene and the propane-propylene fraction of the cracking gas (30% (by volume) propylene and 70% (by volume) propane) for production of 1 ton of phenol if the yield of isopropylbenzene from benzene is 90% of the theoretical and that of phenol from isopropylbenzene is 93% of the theoretical.

Solution. Production of phenol and acetone from benzene and propylene proceeds in three stages:

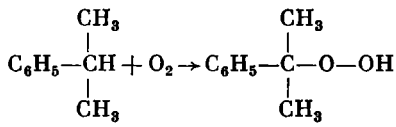
first stage

production of isopropylbenzene (cumene)

$$C_6H_6 + CH_2{=}CH{-}CH_3 \rightarrow C_6H_5{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{CH}}}}$$

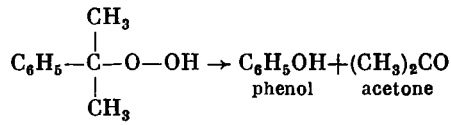
second stage

oxidation of isopropylbenzene to hydroperoxide

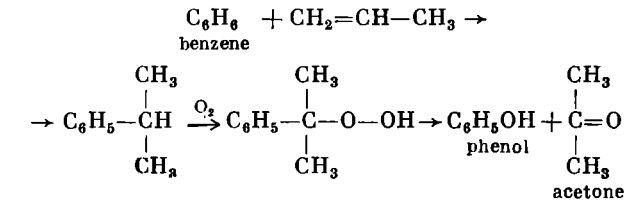


third stage

decomposition of isopropylbenzene hydroperoxide (by boiling with H_2SO_4)



The molecular masses of the compounds: benzene—78, propylene—42, and phenol—94. All the stages of the process can be described by the following scheme:



(a) Production of 1 kmole of phenol requires 1 kmole of benzene so that the theoretical consumption of benzene per 1 ton of phenol is

$$\frac{78 \times 1000}{94} = 830 \text{ kg} = 0.83 \text{ ton}$$

Taking into account the degrees of transformation at the stages of the process we find

$$\frac{0.83}{0.91 \times 0.93} = 0.99 \text{ ton of benzene}$$

(b) Production of 1 kmole of phenol takes 22.4 m^3 of propylene, that is, the volume of propylene needed to produce 1 ton of phenol is

$$V_{th} = \frac{22.4 \times 1000}{94} = 238 \text{ m}^3$$

Or, taking into account the degrees of transformation at the process stages,

$$V_{pr} = \frac{238}{0.91 \times 0.93} = 284 \text{ m}^3$$

The volume of propane accompanying this amount of propylene is

$$\frac{284 \times 70}{30} = 662 \text{ m}^3$$

The total volume of the propane-propylene fraction is

$$284 + 662 = 946 \text{ m}^3$$

Hence the consumption of propylene is

$$\frac{284}{22.4} 42 = 533 \text{ kg}$$

and the consumption of propane is

$$\frac{662}{22.4} 44 = 1300 \text{ kg}$$

The total amount of the propane-propylene fraction needed for production of 1 ton of phenol is 1833 kg $\approx$ 1.83 tons.

Problem 4. Calculate the consumption of the ilmenite ore and sulphuric acid for production of 1 ton of titanium dioxide TiO_2. The ilmenite ore contains $FeTiO_3$ and Fe_2O_3. The titanium content in the ore is 24.3% (by mass). The degree of decomposition of $FeTiO_3$ is 89%. The process utilizes 80% H_2SO_4 in 50% excess of the theoretical amount. Molecular masses: $FeTiO_3$—152, TiO_2—80, Ti—48, Fe_2O_3—159.7, H_2SO_4—98.

Solution. Production of titanium dioxide by treatment of $FeTiO_3$ with sulphuric acid can be described by the following equations:

$$FeTiO_3 + 2H_2SO_4 = (TiO)SO_4 + FeSO_4 + 2H_2O \quad (1)$$

$$(TiO)SO_4 + 2H_2O \rightarrow H_2TiO_3 + H_2SO_4 \quad (2)$$

$$H_2TiO_3 \rightarrow TiO_2 + H_2O \quad (3)$$

Moreover, the iron oxide present in the ore also reacts with sulphuric acid:

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \quad (4)$$

To find the $FeTiO_3$ content in the ilmenite ore first find Ti content in the pure ilmenite:

$$\frac{48 \times 100}{152} = 31.5\%$$

Hence, the ore contains

$$\frac{24.3 \times 100}{31.5} = 78\% \text{ } FeTiO_3$$

The content of Fe_2O_3 in the ore is

$$100 - 78 = 22\% \text{ (by mass)}$$

The consumption of ilmenite $FeTiO_3$ for production of 1 ton of TiO_2 according to reactions (1)-(3) is

$$\frac{152 \times 1000}{80} = 1900 \text{ kg} = 1.9 \text{ tons}$$

The consumption taking into account the degree of decomposition is

$$\frac{1900}{0.89} = 2130 \text{ kg} = 2.13 \text{ tons of ilmenite}$$

The practical consumption coefficient taking into account the composition of the ilmenite ore is

$$A_{pr} = \frac{2.13}{0.78} = 2.74 \text{ tons of ilmenite ore}$$

The consumption of sulphuric acid for decomposition of ilmenite is

$$\frac{1900 \times 98}{152} = 1200 \text{ kg}$$

and the consumption for the reaction (4) with Fe_2O_3 is

$$\frac{0.22 \times 2740 \times 3 \times 98}{159.7} = 1110 \text{ kg}$$

The consumption of sulphuric acid for the reactions (1) and (4) is

$$1200 + 1110 = 2310 \text{ kg}$$

Since the 50% excess of sulphuric acid is used in the process the consumption is

$$2310 \times 1.5 = 3470 \text{ kg}$$

Hence, the consumption of 80% H_2SO_4 is

$$\frac{3470}{0.8} = 4340 \text{ kg}$$

Problem 5. Determine the consumption coefficients for production of calcium carbide (technical grade) with the following composition: CaC_2—78%, CaO—15%, C—3%, other impurities—4%. The coefficients should be calculated for 1 ton of technical-grade product. The lime contains 96.5% CaO. Composition of the coke: ash—4%, volatile components—4%, moisture—3%. Molecular masses: CaC_2—64, CaO—56.

Solution. Calcium carbide is produced according to the equation

$$CaO + 3C = CaC_2 + CO$$

Consumption of lime. 1 ton of the product contains 780 kg of CaC_2; the stoichiometric relationship shows that to produce this amount of CaC_2 we need

$$\frac{780 \times 56}{64} = 675 \text{ kg of CaO}$$

Moreover, the technical-grade product contains unreacted CaO:

$$1000 \times 0.15 = 150 \text{ kg}$$

The consumption of CaO is 675 + 150 = 825 kg and the consumption of lime is

$$A_{pr.1} = \frac{825}{0.965} = 850 \text{ kg}$$

Consumption of coke. The content of carbon in the coke is

$$100 - (4 + 4 + 3) = 89\%$$

The amount of carbon consumed for production of 1 ton of CaC_2 is

$$\frac{780 \times 3 \times 12}{64} = 440 \text{ kg}$$

The final product contains $1000 \times 0.03 = 30$ kg of unreacted carbon.

The carbon consumption is 440 + 30 = 470 kg.

The consumption coefficient for coke is

$$A_{pr.2} = \frac{470}{0.89} = 530 \text{ kg}$$

Problem 6. Find the consumption of the brown coal containing 70% (by mass) carbon, steam and air for production of 1000 m^3 of the producer gas with the following composition (% by volume): CO—40, H_2—18, N_2—42. For simplicity, the air is assumed to contain 79% (by volume) N_2 and 21% (by volume) O_2.

Solution. The process of gasification is the conversion of solid fuel into gaseous fuel owing to treatment with air, steam or their mixture at a high temperature according to the following equations:

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$

$$2C + O_2 \rightarrow 2CO \quad (2)$$

Thus, the producer gas is made by treating the coal with the air-steam mixture.

1000 m^3 of gas are assumed to contain 420 m^3 of nitrogen. Hence, the consumption of oxygen in the reaction (2) is

$$V_{O_2} = \frac{420 \times 21}{79} = 112 \text{ m}^3$$

or

$$\frac{112}{22.4} 32 = 160 \text{ kg}$$

Therefore, the consumption of air is 112 + 420 = 532 m^3 or

$$A_{pr.1} = \frac{532}{22.4} 29 = 700 \text{ kg}$$

where 29 is the molecular mass of the air.

Steam consumption in the reaction (1). The yield of hydrogen is 1 mole per 1 mole of steam. 1000 m^3 of the producer gas contain

180 m³ of hydrogen to produce which 180 m³ of steam are needed or

$$A_{pr.2}=\frac{180}{22.4}18=145 \text{ kg}$$

The consumption of carbon is

$$\frac{12\times180}{22.4}=96.5 \text{ kg in the reaction (1)}$$

and

$$\frac{2\times12\times112}{22.4}=120 \text{ kg in the reaction (2).}$$

The consumption of carbon in both reactions is 96.5 + 120=216.5 kg. Hence, the consumption of the brown coal containing 70% C is

$$A_{pr.3}=\frac{216.5}{0.7}=310 \text{ kg}$$

Problem 7. Calculate the consumption coefficient for the natural gas containing 97% by volume of methane used for production of acetic acid from acetaldehyde (per 1 ton of the product). Acetylene is produced from methane in 15% yield, acetylene gives rise to acetaldehyde in 60% yield and acetic acid is produced from acetaldehyde in 90% (by mass) yield.

Solution. Acetic acid is produced from methane in several stages. The process can be described by the following successive reactions:

$$2CH_4 \rightleftarrows C_2H_2+3H_2$$
$$C_2H_2+H_2O \rightleftarrows CH_3CHO$$
$$CH_3CHO+0.5O_2 \rightleftarrows CH_3COOH$$

Molecular masses: C_2H_2—26, CH_3CHO—44, CH_3COOH—60, CH_4—16. The theoretical consumption of methane for production of 1 ton of acetic acid is $1000 \times 2 \times 16/60 \approx 534$ kg. Taking into account the yields of the process stages we find that the consumption is

$$\frac{534}{0.9\times0.6\times0.15}=6590 \text{ kg}$$

or

$$\frac{6590\times22.4}{16}=9226 \text{ m}^3 \text{ of } CH_4$$

or

$$A_{pr}=\frac{9226}{0.97}=9500 \text{ m}^3 \text{ of natural gas}$$

Problem 8 [13, p. 237]. Determine the consumption of ammonia for production of 100 000 tons of nitric acid per year and the consumption of air for oxidation of ammonia (in m³/h) if the plant is in operation 355 days a year. The yield of nitric oxide is 97%, the

yield of nitric acid is 0.92 and the content of ammonia in the dry ammonia-air mixture is 7.13% by mass.

Solution. The first stage in production of nitric acid from ammonia is the oxidation of ammonia by air oxygen to nitric oxide in the presence of platinum catalyst at 800-900 °C. Then nitric oxide is oxidized to nitrogen dioxide which reacts with water giving rise to nitric acid. The process may be described by the following equations:

$$4NH_3+5O_2=4NO+6H_2O$$
$$2NO+O_2=2NO_2$$
$$3NO_2+H_2O=2HNO_3+NO$$

These equations can be approximated by the following total equation for the material balance calculations:

$$NH_3+2O_2=HNO_3+H_2O$$

The molecular masses: NH_3—17, HNO_3—63.

The amount of ammonia consumed for production of 100 000 tons of HNO_3 allowing for the yields of nitric oxide and nitric acid is

$$\frac{100\,000\times 17}{63\times 0.97\times 0.92}=30\,300 \text{ tons}$$

The per hour consumption of ammonia is

$$\frac{1000\times 30\,300}{355\times 24}=3560 \text{ kg/h}$$

This amount of ammonia has the volume

$$\frac{3560\times 22.4}{17}=4680 \text{ m}^3$$

The consumption of air (in m^3/h) for oxidation of ammonia (in the ammonia-air mixture) is

$$\frac{4680\,(100-11.5)}{11.5}=36\,000 \text{ m}^3/\text{h}$$

Here 11.5 is the content of NH_3 in the mixture (in % by volume):

$$\frac{\frac{7.13}{17}100}{\frac{7.13}{17}+\frac{92.87}{29.0}}=11.5$$

Material Balances for Irreversible Chemical Technological Processes

Problem 9. Draw up the material balance for the furnace burning sulphur (60 tons per 24 hours). The degree of oxidation of sulphur is 0.95 (the remaining sulphur is sublimed and burns outside the

furnace). The excess ratio* for the air is 1.5. Calculate consumption of the materials per hour.

Solution. Burning of sulphur is described by the following equation:

$$S + O_2 = SO_2$$

The consumption of sulphur is

$$\frac{60}{24} = 2.5 \text{ tons/h} = 2500 \text{ kg/h}$$

The amount of sulphur oxidized to SO_2 is

$$2500 \times 0.95 = 2375 \text{ kg/h}$$

The amount of remaining unoxidized sulphur is

$$2500 - 2375 = 125 \text{ kg/h}$$

The consumption of oxygen for oxidation is

$$V_{O_2} = \frac{2375 \times 22.4}{32} = 1663 \text{ m}^3$$

Taking into account the excess ratio we find the actual consumption of oxygen:

$$1663 \times 1.5 = 2.495 \text{ m}^3 \quad \text{or} \quad \frac{2495 \times 32}{22.4} = 3560 \text{ kg/h}$$

The amount of nitrogen fed together with oxygen is

$$V_{N_2} = \frac{2495 \times 79}{21} = 9380 \text{ m}^3/\text{h} \quad \text{or} \quad \frac{9380 \times 28}{22.4} = 11\,700 \text{ kg/h}$$

The amount of sulphur dioxide formed in the reaction is

$$\frac{2375 \times 64}{32} = 4750 \text{ kg/h}$$

or

$$V_{SO_2} = \frac{4750}{64} 22.4 = 1663 \text{ m}^3/\text{h}$$

The amount of remaining unreacted oxygen is

$$1663 \times 0.5 = 831 \text{ m}^3/\text{h} \quad \text{or} \quad \frac{831}{22.4} 32 = 1183 \text{ kg/h}$$

The results are summarized in Table 2.

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* The excess ratio for the air (oxygen) is the ratio of the amount of the air fed to the furnace to the amount theoretically needed according to the equation of the reaction.

TABLE 2

Material Balance for the Sulphur-burning Furnace
(per 1 h)

INPUTS			OUTPUTS		
Materials	kg	m^3	Products	kg	m^3
S	2 500		S	125	
O_2	3 560	2 495	SO_2	4 750	1 663
N_2	11 700	9 380	O_2	1 183	831
			N_2	11 700	9 380
Total:	17 760	11 875	*Total:*	17 758	11 874

Problem 10. Draw up the material balance for production of ethylene oxide by direct catalytic oxidation of ethylene with air. The composition of the starting gas mixture (% by volume): ethylene—3, air—97. The degree of oxidation of ethylene is 0.5. Calculations should be made for production of 1 ton of ethylene oxide.

Solution. Ethylene oxide is a highly important semifinished product which is widely used in chemical industry for synthesizing ethylene glycol, polyglycols, varnish solvents, plasticizers, ethanol amines, various emulsifiers and detergents and the compounds used for production of synthetic fibers, synthetic rubbers, etc.

There are two main methods for production of ethylene oxide.

1. Hypochlorination of ethylene followed by cleavage of hydrogen chloride from the resulting ethylene chlorohydrin.

2. Direct catalytic oxidation of ethylene. A mixture of air and ethylene (the lower limit for explosivity of the ethylene-air mixture is 3.4% C_2H_4 content) passed over a silver catalyst at 250-280 °C gives rise to ethylene oxide:

$$2CH_2=CH_2+O_2=2CH_2-CH_2$$
$$\diagdown\ \diagup$$
$$O$$

Ethylene oxide is isolated from the gas mixture by water absorption and the residual gas is fed into the second reactor.

The consumption of ethylene for production of 1 ton of ethylene oxide can be found from the equation of the reaction. 28 kg of C_2H_4 yield 44 kg of C_2H_4O so that to produce 1 ton of ethylene oxide we need

$$\frac{28 \times 1000}{44} = 640 \text{ kg} \quad \text{of} \quad C_2H_4$$

Since the degree of oxidation is 0.5 the actual ethylene consumption is

$$\frac{640}{0.5} = 1280 \text{ kg} \quad \text{or} \quad \frac{128 \times 22.4}{28} = 1020 \text{ m}^3$$

The volume of air in the ethylene-air mixture corresponding to this amount of ethylene is

$$\frac{1020 \times 97}{3} = 33\,000 \text{ m}^3$$

The respective volume of oxygen is $33\,000 \times 0.21 = 6800$ m³ or $6800 \times 32/22.4 = 9700$ kg and the amount of nitrogen is $33\,000 \times 0.79 = 26\,200$ m³ or $26\,200 \times 28/22.4 = 32\,500$ kg.

The consumption of oxygen for oxidation of ethylene is $1020 \times 0.5/2 = 255$ m³. The amount of oxygen in the oxidation products is $6800 - 255 = 6545$ m³ or $6545 \times 32/22.4 = 9340$ kg. The results are summarized in Table 3.

TABLE 3

Material Balance for Ethylene Oxidation
(per 1 ton C_2H_4O)

INPUTS			OUTPUTS		
Materials	kg	m³	Products	kg	m³
Ethylene	1 280	1 020	Ethylene oxide	1 000	510
Air incl.			Ethylene	640	510
oxygen	9 700	6 800	Oxygen	9 340	6 545
nitrogen	32 500	26 200	Nitrogen	32 500	26 200
Total:	43 480	34 020	*Total*:	43 480	33 765

Problem 11. After electrocracking of the natural gas containing 98% by volume of CH_4 and 2% by volume of N_2 the gas discharged from the apparatus contains 15% of acetylene. Calculate the material balance of the process per 1000 m³ of the natural gas ignoring the side reactions.

Solution. Acetylene is produced from gaseous hydrocarbons (chiefly, from methane) at 1200-1600 °C:

$$2CH_4 \rightleftarrows C_2H_2 + 3H_2 - 380 \text{ kJ}$$

The process is carried out in electric arc furnaces at 1600 °C and with gas velocity of 1000 m/s.

1000 m³ of natural gas contain 980 m³ of CH_4 and 20 m³ of N_2. The process results in a change of the volume. According to the equation of the reaction if methane is completely transformed into acetylene the mixture of the products should contain 25% of acetylene.

Since the actual acetylene content is 15% this means that the decomposition of methane is incomplete.

Denote by x the volume (in m^3) of the transformed methane. Then the mixture of the products has the following composition:

CH_4	$980-x$
C_2H_2	$x/2$
H_2	$(3/2)x$
N_2	20
Total	$(1000+x)m^3$

The acetylene content in the products is 15%, that is,

$x/2$	15%
$1000+x$	100%

Hence we obtain

$$(x/2)\ 100/(1000 + x) = 15$$

Thus, $x = 430$ m^3 and the gas products after cracking have the following composition (per 1000 m^3 of natural gas): C_2H_2—215 m^3, H_2—645 m^3, CH_4—550 m^3, and N_2—20 m^3.

The results are summarized in Table 4.

TABLE 4

Material Balance for Cracking of Natural Gas (per 1000 m^3 of Natural Gas)

INPUTS				OUTPUTS			
Materials	m^3	kg	% by volume	Products	m^3	kg	% by volume
CH_4	980	695	98	C_2H_2	215	248	15.0
N_2	20	25	2	CH_4	550	388	38.5
				H_2	645	58	45.0
				N_2	20	25	1.5
Total:	1000	720	100	*Total:*	1430	719	100

Problem 12. Calculate the material balance for the oxidizing roasting furnace producing sodium vanadate (per 1 ton of the final product $NaVO_3$). Raw materials—vanadium slag containing 13% (by mass) of V_2O_5, air, and NaCl (10% by mass of the slag mass).

Solution. Vanadium is used for manufacturing hard alloys, special steels, and cast iron. Vanadium compounds are used as catalysts in production of sulphuric acid and aniline dyes, for oxidation of naphthalene, and so on. Melting of iron-vanadium ores in blast furnaces produces vanadium-containing pig iron. When steel is

produced from such pig iron the resulting slags contain up to 15-18% V_2O_5 and can be used as raw material for vanadium production.

To isolate vanadium the vanadium-containing raw material (ore, slag, concentrate) is mixed with a small amount of sodium chloride, crushed and subjected to oxidizing roasting at 800-900 °C in rotary furnaces. The process can be assumed to consist of two stages:
first stage

$$2NaCl+\frac{1}{2}O_2=Na_2O+Cl_2$$

second stage

$$Na_2O+V_2O_5=2NaVO_3$$

Molecular masses: $NaVO_3$—122, V_2O_5—182, Na_2O—62, NaCl—58.5.

The amount of V_2O_5 needed for production of 1 ton of $NaVO_3$ is $1000 \times 182/244 = 745$ kg corresponding to $745/0.13 = 5600$ kg of vanadium slag. The amount of sodium chloride is 10% of the mass of the vanadium slag—$5600 \times 0.1 = 560$ kg.

The consumption of NaCl for production of 1 ton of $NaVO_3$ (molecular mass $2 \times 58.5 = 117$) is $117 \times 1000/244 = 480$ kg. The amount of unreacted NaCl is $560 - 480 = 80$ kg. The consumption of oxygen is $16 \times 480/117 = 65.5$ kg or $65.5 \times 22.4/32 = 45.8$ m³. The amount of nitrogen fed together with oxygen is $45.8 \times 79/21 = 172$ m³ or $172 \times 28/22.4 = 214$ kg. The amount of chlorine produced at the first stage of the process is $71 \times 1000/244 = 290$ kg. The results are summarized in Table 5.

TABLE 5

Material Balance for Oxidizing Roasting Furnace
(per 1 ton $NaVO_3$)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
Vanadium slag	5600	Slime	4855
NaCl	560	$NaVO_3$	1000
Air, incl.		NaCl	80
O_2	65.5	Cl_2	290
N_2	214	N_2	214
Total:	6439.4	*Total*:	6439.0

Problem 13. Calculate the material balance (per 1 ton) for production of cryolite described by the following overall reaction equation:

$$2Al(OH)_3+12HF+3Na_2CO_3=2Na_3AlF_6+3CO_2+9H_2O$$

The reaction is carried out with 15% water solution of hydrofluoric acid. The amount of sodium carbonate is 4% less than the stoichiometric amount in order to provide for the required residual acidity.

Solution. Cryolite Na_3AlF_6 is a component material in production of aluminium. Cryolite is produced in a lead reactor with a stirrer heated with live steam to 50-70 °C. Aluminium hydroxide and 12-15% hydrofluoric acid are loaded into the reactor and after dissolving sodium carbonate is added. The residual acidity should be about 2 g/litre.

The cryolite sediment is filtered off, washed and dried in a drier heated from the outside with flue gas with the temperature not more than 400 °C. The reactions leading to the formation of cryolite can be described by the following equations:

$$2Al(OH)_3+12HF=2H_3AlF_6+6H_2O \quad (1)$$

$$2H_3AlF_6+3Na_2CO_3=2Na_3AlF_6+3CO_2+3H_2O \quad (2)$$

Molecular masses: $Al(OH)_3$—78, HF—20, Na_2CO_3—106, H_3AlF_6—144, Na_3AlF_6—210.

According to the reaction equations the following amounts of materials are needed to obtain 1 ton of cryolite: $Al(OH)_3$—$2 \times 78 \times 1000/2 \times 210 = 371$ kg; HF—$12 \times 20 \times 1000/2 \times 210 = 572$ kg or 15% HF solution—$572/0.15 = 3810$ kg; Na_2CO_3—$3 \times 106 \times 1000/2 \times 210 = 758$ kg. The amount of water needed for the hydrofluoric acid solution is 3810— 572 = 3238 kg. To provide for the excess acidity of the solution additional amounts of $Al(OH)_3$ and HF should be loaded to the reactor. The amount of Na_2CO_3 equivalent to the excess acidity is $758 \times 0.04 = 32.7$ kg. According to Eq. (2) the amount of H_3AlF_6 equivalent to 32.7 kg of Na_2CO_3 is $2 \times 144 \times 32.7/3 \times 106 = 29.6$ kg. According to Eq. (1) to obtain this amount of acid we need $2 \times 78 \times 29.6/2 \times 144 = 16$ kg of $Al(OH)_3$ and $12 \times 20 \times 29.6/2 \times 144 = 24.6$ kg of HF or $24.6/0.15 = 164$ kg of 15% HF. The respective amount of H_2O is $164 - 24.6 = 139.4$ kg.

Hence, the final results taking into account the excess acidity requirement are:

$Al(OH)_3$	$371+16=387$ kg
HF	$572+24.6=596.6$ kg
H_2O	$3238+139.4=3377.4$ kg
Na_2CO_3	758 kg

The mixture of products contains the following amounts:

Na_3AlF_6	1000 kg
H_3AlF_6	29.6 kg
CO_2	$3 \times 44 \times 1000/2 \times 210 = 314$ kg
H_2O (reaction product)	$9 \times 18 \times 1000/2 \times 210 = 386$ kg
H_2O (in hydrofluoric acid solution)	3377.4 kg

The results are summarized in Table 6.

TABLE 6

Material Balance for the Cryolite-producing Reactor (per 1 ton)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
$Al(OH)_3$	387	Na_3AlF_6	1000
HF } 15%	596.6	H_3AlF_6	29.6
H_2O } solution	3377.4	CO_2	314
Na_2CO_3	758	H_2O (reaction product)	386
		H_2O (in HF solution)	3377.4
Total:	5114	*Total:*	5102

Problem 14. Calculate the material balance for a chlorinator producing chlorobenzene (per 1 ton of chlorobenzene). The composition of the liquid products (% by mass): benzene—65.0, chlorobenzene—32.0, dichlorobenzene—2.5, and trichlorobenzene—0.5. The commercial grade benzene contains 97.5% by mass of C_6H_6. The technical-grade chlorine contains 98% by mass of Cl_2.

Solution. Chlorobenzene is used for producing such benzene derivatives as phenol, aniline, etc. Chlorobenzene is produced by passing chlorine through liquid benzene in the presence of iron(III) chloride. Formation of chlorobenzene according to the main reaction equation

$$C_6H_6+Cl_2 \rightarrow C_6H_5Cl+HCl \quad (1)$$

is accompanied by further chlorination reactions:

$$C_6H_5Cl+Cl_2 \rightarrow C_6H_4Cl_2+HCl$$

or

$$C_6H_6+2Cl_2 \rightarrow C_6H_4Cl_2+2HCl \quad (2)$$
$$C_6H_4Cl_2+Cl_2 \rightarrow C_6H_3Cl_3$$

or

$$C_6H_6+3Cl_2 \rightarrow C_6H_3Cl_3+3HCl \quad (3)$$

To prevent formation of polychlorides in large amounts chlorination should be stopped when a little less than half of benzene has reacted (when the reaction mixture contains 60-65% of unreacted benzene). Molecular masses: C_6H_6—78, C_6H_5Cl—112.5, $C_6H_4Cl_2$—147, $C_6H_3Cl_3$—181.5, Cl_2—71, HCl—36.5.

The content of the liquid reaction products per 1000 kg of C_6H_5Cl: $C_6H_4Cl_2$—$1000 \times 2.5/32 = 78$ kg, $C_6H_3Cl_3$—$1000 \times 0.5/32 = 15.6$ kg.

The mixture of products also contains hydrogen chloride in the following amounts: reaction (1)—$1000 \times 36.5/112.5 = 324$ kg; reaction (2)—$78 \times 2 \times 36.5/147 = 39$ kg; reaction (3)—$15.6 \times 3 \times \times 36.5/181.5 = 9.4$ kg. The total amount of hydrogen chloride in the product mixture is 372.4 kg.

The consumption of pure benzene for production of 1 ton of C_6H_5Cl is found by adding the following amounts:
consumed for production of C_6H_5Cl—$1000 \times 78/112.5 = 693$ kg
consumed for production of $C_6H_4Cl_2$—$78 \times 78/147 = 41$ kg
consumed for production of $C_6H_3Cl_3$—$15.6 \times 78/181.5 = 6.7$
unreacted benzene—$1000 \times 65/32 = 2031.0$ kg

The total consumption of benzene is 2771.7 kg. The consumption of technical-grade benzene is $2771.7/0.975 = 2842.8$ kg.

The consumption of chlorine for production of 1 ton of C_6H_5Cl is found by adding the following amounts:
consumed for production of C_6H_5Cl—$1000 \times 71/112.5 = 631$ kg
consumed for production of $C_6H_4Cl_2$—$78 \times 2 \times 71/147 = 75$ kg
consumed for production of $C_6H_3Cl_3$—$15.6 \times 3 \times 71/181.5 = 18.3$ kg

The total consumption of chlorine is 724.3 kg. The consumption of technical-grade chlorine is $724.3/0.98 = 739$ kg. The results are summarized in Table 7.

TABLE 7

Material Balance for Chlorator of Benzene
(per 1 ton of chlorobenzene)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
Technical-grade benzene, incl.		C_6H_5Cl	1000
pure benzene	2771.7	$C_6H_4Cl_2$	78
impurities	71.1	$C_6H_3Cl_3$	15.6
Technical-grade chlorine, incl.		C_6H_6	2031
		HCl	372.4
		C_6H_6 impurities	71.1
pure chlorine	724.3	Cl_2 impurities	14.7
impurities	14.7		
Total:	3581.8	*Total*:	3582.8

Problem 15. Calculate the material balance for production of hydrogen fluoride (per 1 ton of HF) from fluorite containing 96% CaF_2 and 4% SiO_2. The degree of decomposition of fluorite is 0.95. The reaction is carried out with 93% H_2SO_4 in 15% excess of the theoretical amount.

Solution. Production of HF involves the following reactions:

$$CaF_2+H_2SO_4=CaSO_4+2HF \quad (1)$$

$$SiO_2+6HF=H_4SiF_6+2H_2O \quad (2)$$

Hydrogen fluoride is dissolved in water and the resulting hydrofluoric acid is used in production of fluorides, for organic syntheses, for etching glass, and so on. Molecular masses: CaF_2—78, H_2SO_4—98, $CaSO_4$—136, HF—20, SiO_2—60, and H_2SiF_6—144.

100 kg of fluorite contain 96 kg of CaF_2 and 4 kg of SiO_2. The reaction with sulphuric acid gives rise to HF (reaction (1)) and a part of HF reacts with SiO_2 giving rise to H_2SiF_6. Hence, for 100 kg of fluorite the amount of HF formed in the reaction (1) is $96 \times 20 \times 2/78 = 49$ kg and the consumption of HF in the reaction (2) is $6 \times 20 \times 4/60 = 8$ kg. The total amount of HF obtained from 100 kg of fluorite is $49 - 8 = 41$ kg, that is, to produce 1 ton of HF we need $100 \times 1000/41 = 2440$ kg of fluorite consisting of 2340 kg of CaF_2 and 100 kg of SiO_2. Since the degree of decomposition of fluorite in the process is 0.95 the consumption of fluorite is $2440/0.95 = 2570$ kg including 2467 kg of CaF_2 and 103 kg of SiO_2.

The amount of sulphuric acid required for the reaction (1) is $98 \times 2340/78 = 2950$ kg. Since the acid is taken in 15% excess the required amount is $2950 \times 1.15 = 3400$ kg and the consumption of 93% H_2SO_4 is $3400/0.93 = 3640$ kg.

The amount of water in the acid solution is $3640 - 3400 = 240$ kg.

The composition of the product mixture: $CaSO_4$—$2340 \times 136/78 = 4050$ kg, H_2SiF_6—$144 \times 100/60 = 240$ kg, and H_2O (reaction product)—$36 \times 100/60 = 60$ kg. The results are summarized in Table 8.

TABLE 8

Material Balance for the Reactor Producing Hydrogen Fluoride
(per 1 ton of HF)

INPUTS			OUTPUTS	
Materials		kg	Products	kg
Fluorite	CaF_2	2467	HF	1000
	SiO_2	103	$CaSO_4$	4050
H_2SO_4 (pure)		3400	H_2SiF_6	240
H_2O in H_2SO_4 solution		240	H_2O (reaction product)	60
			H_2O (in H_2SO_4 solution)	240
			H_2SO_4	450
			CaF_2	127
			SiO_2	3
Total:		6210	*Total:*	6170

Problem 16. Calculate the material balance for the roasting furnace producing clinker for Portland cement (per 1 ton of the clinker). The charge contains 20% of building clay and 80% of limestone which have the following compositions (in % by mass): building clay: SiO_2—72.0, Al_2O_3—16.0, Fe_2O_3—7.0, K_2O—1.7, Na_2O—3.3; limestone: $CaCO_3$—95.0, impurities—5.0.

Solution. Portland cement is a widely used hydraulic cement which is distinguished by high strength and water and frost resistance. These properties of the Portland cement are determined by the oxide composition comprising the cement clinker. The components of the charge for clinker production are finely ground, carefully mixed, and roasted in rotary kilns. When moisture has evaporated the minerals of the clay are dehydrated (at about 500 °C) and then lime yields calcium oxide which reacts with clay components giving rise to calcium silicates and other compounds.

Clinkering of materials occurs at 1400-1450 °C:

$$CaCO_3 \rightarrow CaO + CO_2$$

In the process, CaO, SiO_2, Al_2O_3, and Fe_2O_3 give rise to the following compounds: $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. Molecular masses: $CaCO_3$—100, CaO—56, and CO_2—44.

From the composition of the charge and the chemical compositions of clay and limestone we can calculate the content of the compounds (in %) in the charge: $CaCO_3$—$80 \times 0.95 = 76.0$, SiO_2—$20 \times 0.72 = 14.4$, Al_2O_3—$20 \times 0.16 = 3.2$, Fe_2O_3—$20 \times 0.07 = 1.4$, K_2O—$20 \times 0.017 = 0.34$, Na_2O—$20 \times 0.033 = 0.66$, impurities—$80 \times 0.05 = 4.00$ (total = 100%).

Owing to decomposition $CaCO_3 \rightarrow CaO + CO_2$ the composition of the clinker is changed. 100 kg of the charge produce clinker with the following composition (in kg): CaO—$76 \times 56/100 = 43$, SiO_2—14.4, Al_2O_3—3.2, Fe_2O_3—1.4, K_2O—0.34, Na_2O—0.66, impurities—4.00. The total amount is 67 kg of clinker and 33 kg of CO_2. The clinker has the following composition (in % by mass): CaO—$43 \times 100/67 = 64.2$, SiO_2—$14.4 \times 100/67 = 21.5$, Al_2O_3—$3.2 \times 100/67 = 4.71$, Fe_2O_3—$1.4 \times 100/67 = 2.08$, K_2O—$0.34 \times 100/67 = 0.51$, Na_2O—$0.66 \times 100/67 = 1.00$, impurities—$4 \times 100/67 = 6.00$.

The consumption of materials for production of 1 ton of clinker: calcium carbonate—$642 \times 100/56 = 1170$ kg, limestone—$1170/0.95 = 1230$ kg. The amount of impurities in the limestone is $1230 - 1170 = 60$ kg. The consumption of clay components (kg): SiO_2—215, Al_2O_3—47.1, Fe_2O_3—20.8, K_2O—5.1, Na_2O—10.0, total—298.0. The calculation results are given in Table 9.

Problem 17 (taken from [13], p. 237, with some modifications). Calculate the material balance for the plant producing nitric acid from ammonia (per 1 ton of nitric acid). The degree of oxidation of

TABLE 9

Material Balance of the Kiln for Cement Clinker Production
(per 1 ton)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
Limestone:		Clinker:	1000
$CaCO_3$	1170	CaO	642
Impurities	60	SiO_2	215
Clay:		Al_2O_3	47.1
SiO_2	215	Fe_2O_3	20.8
Al_2O_3	47.1	K_2O	5.1
Fe_2O_3	20.8	Na_2O	10
K_2O	5.1	Impurities	60
Na_2O	10.0	CO_2	528
Total:	1528	*Total*:	1528

ammonia to NO is 0.97 and the yield of N_2 is 0.03. The yield of NO_2 from NO is 1.0 and the yield of nitric acid is 0.92. The content of ammonia in the dry ammonia—air mixture is 7.13% by mass. The air is saturated with water vapour at 30 °C. The relative humidity is 80%.

Solution. Nitric acid is produced by oxidizing ammonia with the oxygen of the air and treating the resulting nitrogen oxides.

The balance equation for production of nitric acid from ammonia can be written as follows:

$$NH_3+2O_2=HNO_3+H_2O+411.2 \text{ kJ/mole}$$

Ammonia is oxidized to nitric oxide over a platinum or chromium oxide catalyst. Then NO is oxidized to NO_2 which reacts with water producing nitric acid.

According to the balance equation 1 kmole of NH_3 yields 1 kmole of HNO_3. The amount of ammonia needed to produce 1 ton of HNO_3 is $1 \times 17/63 \times 0.97 \times 0.92 = 0.303$ ton $= 303$ kg. Molecular masses: HNO_3—63, NH_3—17. The volume of this amount of ammonia is $303 \times 22.4/17 = 400$ m³.

The consumption of air per 1 ton of nitric acid is

$$303\ (100 - 7.13)/7.13 = 3950 \text{ kg}$$

or

$$3950 \times 22.4/29.0 = 3070 \text{ m}^3$$

(here 29.0 is the molecular mass of the air). This amount of air contains $3070 \times 21/100 = 645$ m³ or $645 \times 32/22.4 = 923$ kg of

oxygen and $3070 \times 79/100 = 2425$ m³ or $2425 \times 28/22.4 = 3030$ kg of nitrogen. The volume of the dry gases is 3070 m³. The partial pressure of water vapour at 30 °C and the relative humidity 80% is $0.8 \times 4.22 \times 10^3 = 3.37 \times 10^3$ Pa (here 4.22×10^3 Pa is the pressure of the water vapour at 100% relative humidity at 30 °C). Hence, the amount of water fed with the air and ammonia is

$$3070 \times 3.37 \times 10^3/(101 - 3.37) \times 10^3 = 105 \text{ m}^3$$

or

$$105 \times 18/22.4 = 84.5 \text{ kg}$$

Now find the composition of the nitrogen gases. The reaction

$$4NH_3+5O_2=4NO+6H_2O$$

yields $400 \times 0.97 = 388$ m³ or $388 \times 30/22.4 = 518$ kg of NO and $388 \times 6/4 = 582$ m³ or $528 \times 18/22.4 = 468$ kg of water vapour. The consumption of oxygen in this reaction is $388 \times 5/4 = 485$ m³ or $485 \times 32/22.4 = 693$ kg.

The reaction

$$4NH_3+3O_2=2N_2+6H_2O$$

gields $400 \times 0.03 \times 2/4 = 6$m³ or $6 \times 28/22.4 = 7.5$ kg of nitroyen and $400 \times 0.03 \times 6/4 = 18$ m³ or $18 \times 18/22.4 = 14.5$ kg of water vapour. The consumption of oxygen in this reaction is $400 \times 0.03 \times 3/4 = 9$ m³ or $9 \times 32/22.4 = 12.7$ kg.

Hence, the nitrogen gases have the following composition:

	kg	m³	% by volume
NO	518.0	388	10.3
O_2	$923-693-12.7=217.3$	152	4.1
N_2	$3030+7.5=3037.5$	2430	66.1
H_2O	$14.5+468+84.5=567$	706	19.1

The results are summarized in Table 10.

TABLE 10

Material Balance for Nitric Acid Production
(per 1 ton HNO_3)

INPUTS			OUTPUTS		
Materials	kg	m³	Products	kg	m³
NH_3 air mixture, incl.			Nitrogen gases, incl.		
NH_3	303	400	NO	518	388
O_2	923	645	O_2	217.3	152
N_2	3030	2425	N_2	3037.5	2430
H_2O	84.5	105	H_2O	567	706
Total: 4340.5			*Total:*	4339.8	

Problem 18. Calculate the material balance per 1 ton of the production of the iron trioxide catalyst. *Materials*: hydrous ferrous sulphate $FeSO_4 \cdot 7H_2O$ used as the 2 N solution with the density 1152 kg/m³, 25% ammonia water (10% ammonia solution is used in the process).

Solution. Production of iron trioxide catalyst is carried out in the following stages: treatment of the hydrous ferrous sulphate solution with ammonia water giving rise to $Fe(OH)_2$, oxidation of $Fe(OH)_2$ to $Fe(OH)_3$, and roasting of $Fe(OH)_3$ producing the end product. The process can be described by the following reaction equations:

$$2FeSO_4 + 4NH_3 + 4H_2O = 2Fe(OH)_2 + 2(NH_4)_2SO_4$$

$$2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 = 2Fe(OH)_3$$

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

$$2FeSO_4 + 4NH_3 + 2H_2O + \frac{1}{2} O_2 = Fe_2O_3 + 2(NH_4)_2SO_4$$

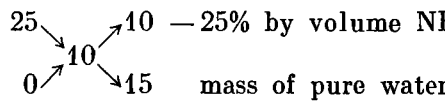
The consumption of ferrous sulphate:

$$\underset{2\times278}{2FeSO_4 \cdot 7H_2O} \rightarrow \underset{2\times152}{2FeSO_4} \rightarrow \underset{160}{Fe_2O_3}$$

The consumption of hydrous ferrous sulphate for production of 1 ton of Fe_2O_3 is $1000 \times 2 \times 278/160 = 3480$ kg. 1 m³ of 2 N solution of hydrous ferrous sulphate contains 1 kmole or 278 kg of sulphate so that the consumption of the 2 N solution is $3480/278 = 12.5$ m³ or $12.5 \times 1152 = 14\,500$ kg including $152 \times 12.5 = 1900$ kg of $FeSO_4$ and $126 \times 12.5 = 1580$ kg of crystal water. The amount of water needed to prepare the required amount of the 2 N sulphate solution is $14\,500 - (1900 + 1580) = 11\,020$ kg.

The amount of ammonia needed to obtain the required amount of $Fe(OH)_2$ can be found from the ratio $Fe_2O_3 : 4NH_3$; it is $4 \times 17 \times 1000/160 = 425$ kg and the respective amount of 25% ammonia water is $425/0.25 = 1700$ kg.

The amount of water needed to dilute the 25% ammonia solution to 10% solution can be found using the "rule of cross":



Hence, the amount of water needed to dilute 1700 kg of 25% NH_3 is $15 \times 1700/10 = 2570$ kg. The amount of 10% NH_3 solution is $1700 + 2550 = 4250$ kg. The amount of water in the ammonia solution is $4250 - 425 = 3825$ kg. The amount of oxygen needed to oxidize $Fe(OH)_2$ is $16 \times 1000/160 = 100$ kg.

The products of the process are $2(NH_4)_2SO_4$ (2 × 132) and Fe_2O_3 (160). The amount of $(NH_4)_2SO_4$ per 1 ton of Fe_2O_3 is 2 × 132 × × 1000/160 = 1650 kg. According to the overall reaction equation the consumption of water is 2 × 18 × 1000/160 = 225 kg. The amount of water in the filtrate plus the amount of water evaporated by roasting is 11 020 + 3825 + 1580 — 225 = 16 200 kg.

The results are presented in Table 11.

TABLE 11

Material Balance for Iron Trioxide Production
(per 1 ton Fe_2O_3)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
$FeSO_4 \cdot 7H_2O$, incl.		Fe_2O_3	1000
$FeSO_4$	1 900	$(NH_4)_2SO_4$	1650
7 H_2O	1 580	H_2O (filtrate and vapour)	16 200
H_2O (in solution)	11 020		
10% NH_3 solution, incl.			
NH_3	425		
H_2O	3 825		
Oxygen	100		
Total:	18 850	*Total*:	18 850

Problem 19. Calculate the material balance for the furnace burning 200 tons of pyrite per day. Pyrite contains 41% sulphur and 3% moisture. The sulphur content of the pyrite cinders is 1%. The dry flue gas contains 14.1% SO_2 and 2.4% O_2. The temperature of the air fed to the furnace is 20 °C and its relative humidity is 50%.

Solution. The fluid-bed furnace for pyrite roasting typically has the combustion chamber at the bottom of which air is fed at such a rate that the fluidized bed of suspended finely ground pyrite is created providing for good mixing of pyrite and air and hence for high intensity of roasting. The overall reaction can be described by the following equation:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 \quad (1)$$

Owing to high combustion rate and intense mixing the fluidized bed contains pyrite cinders rather than pyrite. The typical sulphur content in the pyrite cinders is 0.5-1%. The height of the fluidized bed depends on the productivity of the furnace and can be as large as 1-1.25 m.

The advantage of the fluidized-bed roasting of pyrite is the production of gas with high SO_2 content (12-15%) and low content of sulphur trioxide.

The balance will be calculated for 1 hour of furnace operation. The consumption of pyrite is 200 000/24 = 8334 kg/h. The amount of moisture in pyrite is 8334 × 0.03 = 250 kg/h. The consumption of dry pyrite is 8334 — 250 = 8084 kg/h.

The amount of pyrite cinders can be found using the formula

$$x_c = \frac{160 - n}{160 - m}$$

where x_c is the yield of pyrite cinders (in kg/kg), n is the content of sulphur in pyrite (%), and m is the content of sulphur in pyrite cinders (%).

According to reaction equation (1) when pyrite cinders are produced 8 sulphur atoms are replaced by 6 oxygen atoms. Hence, 1 kg of S is replaced by 6 × 16/8 × 32 = 3/8 kg of O_2.

If $x = 100x_c$ is the yield of pyrite cinders per 100 kg of pyrite the amount of suphur burned per 100 kg of pyrite is $n - mx$ and the amount of oxygen which replaced this sulphur is 3/8 $(n - mx)$.

Hence, when 100 kg of pyrite are burned producing cinders the amount of sulphur burned is $(n - mx)$ kg and the respective amount of oxygen is 3/8 $(n - mx)$.

The yield of pyrite cinders per 100 kg of pyrite is

$$x = 100 - (n - mx_c) + 3/8\,(n - mx_c) = 100 - (5/8)n + (5/8)\,mx_c$$

or

$$100x_c = 100 - (5/8)\,n + (5/8)\,mx_c,$$

$$x_c = (100 - (5/8)\,n)/(100 - (5/8)\,m) = (160 - n)/(160 - m)$$

The sulphur content in the dry pyrite is 41 × 100/(100 — 3) = = 42.3%. The yield of pyrite cinders is $x_c = (160 - 42.3)/(160 - 1) =$ = 0.74 kg/kg. The amount of the pyrite cinders is 8084 × 0.74 = = 6000 kg/h.

Since we have no data on the excess of air in the furnace the consumption of the air can be calculated from the amount of nitrogen in the flue gas which is equal to that in the incoming air.

First, determine the amount of burned sulphur and the amount of SO_2. Pyrite cinders contain 1% sulphur or 6000 × 0.01 = 60 kg. The amount of sulphur in pyrite is 8084 × 0.423 = 3420 kg. The amount of burned sulphur is 3420 — 60 = 3360 kg. The amount of SO_2 ($S + O_2 = SO_2$) is 3360 × 22.4/32 = 2360 m^3. The total volume of the flue gas is 2360 × 100/14.1 = 16 700 m^3. The content of oxygen in the flue gas is 16 700 × 0.024 = 400 m^3 or 400 × × 32/22.4 = 572 kg. The content of SO_2 in the flue gas is 2360 × × 64/22.4 = 6740 kg. The amount of nitrogen in the flue gas is

16 700 — 2360 — 400 = 12 940 m^3 or 12 940 × 28/22.4 = 17 400 kg. Hence, the amount of the dry air fed to the furnace is 12 940 × × 100/79 = 17 700 m^3 or 17 700 × 1.293 = 22 900 kg (here 1.293 kg/m^3 is the density of the air).

The partial pressure of the saturated water vapour in the air at 20 °C is 2.5 × 10^3 Pa. At the relative humidity of 50% the partial pressure of the water vapour in the air is 2,5 × 10^3 × 0.5 = 1.25 × × 10^3 Pa. The content of the water vapour is

$$17\,700 \times 1.25 \times 10^3/(101 - 1.25) \times 10^3 = 204 \text{ m}^3$$

or

$$204 \times 18/22.4 = 164 \text{ kg}$$

The total mass of the water vapour in the flue gas is 250 + 164 = = 414 kg.

The results are summarized in Table 12.

TABLE 12

Material Balance for Pyrite Combustion
(per 1 hour)

INPUTS			OUTPUTS		
Materials	kg	m^3	Products	kg	m^3
Dry pyrite	8 084	—	Pyrite cinders	6 000	—
Pyrite moisture	250	—	SO_2	6 740	2 360
Dry air	22 900	17 700	O_2	572	400
Air moisture	164	204	N_2	17 400	12 900
			H_2O	414	516
Total:	31 398		*Total*:	31 126	

The difference between inputs and outputs is 100 (31 398 — — 31 126)/31 398 = 0.875%, which is admissible.

Table 13 presents the data on the composition of the flue gas.

TABLE 13

The Composition of the Flue Gas

Humid gas	m^3	% by volume	Dry gas	m^3	% by volume
SO_2	2 360	13.7	SO_2	2 360	14.1
O_2	400	2.3	O_2	400	2.4
N_2	12 940	81.0	N_2	12 940	83.5
H_2O	516	3.0			
Total:	17 216	100	*Total*:	16 700	100

Problem 20. Calculate the material balance for the reactor used for catalytic oxidation of methanol to formaldehyde which produces 10 000 tons of CH_2O per year. The yield of CH_2O from methanol is 0.7 and the overall degree of conversion of methanol is 0.8 taking into account the side reactions. The methanol-air mixture contains 40 % by volume of methanol. The molar ratio of the by-products HCOOH, CO_2, CO, and CH_4 is 1.8 : 1.6 : 0.1 : 0.3. The plant is in operation 341 days a year (the remaining days are reserved for maintenance work and idle periods). Methanol is oxidized over the solid silver catalyst at 600 °C. The material balance should be calculated.

Solution. Owing to its extremely high reactivity formaldehyde is extensively used in organic syntheses, particularly, in production of synthetic resins.

The main process for production of formaldehyde is oxidation of methanol with air over the silver catalyst at 550-600 °C. The process involves two simultaneous reactions—dehydration and oxidation of methanol:

$$CH_3OH + \frac{1}{2} O_2 = CH_2O + H_2O + Q \quad (1)$$

$$CH_3OH = CH_2O + H_2 - Q \quad (2)$$

Typically, the amount of air fed to the reactor is only 80% of that required by the molar ratio $CH_3OH : O_2 = 2 : 1$ and the process involves incomplete combustion of hydrogen liberated in the dehydration reaction:

$$H_2 + \frac{1}{2} O_2 = H_2O + Q \quad (3)$$

The mixture of products leaving the reactor contains 20-21% formaldehyde, 36-38% nitrogen and the impurities CO, CO_2, CH_4, H_2, CH_3OH, HCOOH, etc. These impurities are produced in the following reactions:

$$CH_3OH = CO + 2H_2 \quad (4)$$

$$CH_3OH + H_2 = CH_4 + H_2O \quad (5)$$

$$CH_3OH + O_2 = HCOOH + H_2O \quad (6)$$

$$CH_3OH + 1.5O_2 = CO_2 + 2H_2O \quad (7)$$

The mixture of products is cooled down to 60 °C and fed to the absorption tower washed with water. The resulting formaldehyde solution contains 10-12% methanol which is a desirable impurity in this case as it inhibits polymerization of formaldehyde.

The productivity of the reactor for methanol oxidation is 10 000 × × 1000/341 × 24 = 1220 kg/h of CH_2O or 1220/30 = 40.7 kmole/h.

The amount of methanol required to produce this amount of formaldehyde is $1220 \times 32/30 \times 0.7 = 1860$ kg or $1860/32 = 58.12$ kmole (according to reaction equations (1) and (2) production of 1 mole of formaldehyde requires 1 mole of methanol and the reaction yield is 0.7; 30 and 32 are the molecular masses of formaldehyde and methanol).

The volume of methanol vapour is $1860 \times 22.4/32 = 1300$ m³ and the volume of the air-methanol mixture is $1300/0.4 = 3250$ m³. The volume of air in the mixture is $3250 - 1300 = 1950$ m³ including $1950 \times 0.21 = 410$ m³ of oxygen (586 kg) and $1930 \times 0.79 = 1540$ m³ of nitrogen (1920 kg).

The mixture of products contains the gases of CH_2O, unreacted CH_3OH, nitrogen, and the by-products HCOOH, CO_2, CO, CH_4, H_2, as well as the water vapour. The yield of CH_2O is 40.7 kmole/h. Let us find the amount of methanol consumed for production of the by-products HCOOH, CH_4, CO and CO_2. In the reactions (4)-(7) production of 1 mole of any of these by-products requires 1 mole of methanol. The total consumption of methanol for the side reactions is $58.12 \times 0.8 - 40.7 = 5.8$ kmole. The amount of unreacted methanol in the mixture of products is $58.12 \times 0.2 = 11.6$ kmole or 372 kg. According to the given molar ratio HCOOH : CO_2 : CO : $CH_4 = 1.8 : 1.6 : 0.1 : 0.3$ (total—3.8) the following amounts of the by-products are obtained:

$$\text{HCOOH } 5.8 \times 1.8/3.8 = 2.75 \text{ kmole or } 126.5 \text{ kg}$$
$$CO_2 \; 5.8 \times 1.6/3.8 = 2.45 \text{ kmole or } 108 \text{ kg}$$
$$CO \; 5.8 \times 0.1/3.8 = 0.158 \text{ kmole or } 4.3 \text{ kg}$$
$$CH_4 \; 5.8 \times 0.3/3.8 = 0.459 \text{ kmole or } 7.3 \text{ kg}$$

To determine the amount of the water vapour and hydrogen in the product gases let us calculate the balances for oxygen and hydrogen.

Balance for oxygen. The amount of oxygen fed into the reactor: with air—586 kg; with CH_3OH—$1860 \times 16/32 = 930$ kg; the total is 1516 kg of oxygen.

The consumption of oxygen: formation of CH_2O—$1220 \times 16/30 = 650$ kg, formation of HCOOH—$126.5 \times 32/46 = 88$ kg, formation of CO_2 — $108 \times 32/44 = 78.6$ kg, formation of CO—$4.3 \times 16/28 = 2.45$ kg. The amount of oxygen in the unreacted methanol is $372 \times 16/32 = 186$ kg. The total consumption of oxygen is $650 + 88 + 78.6 + 2.4 + 186 = 1005$ kg.

The remaining amount of oxygen which is $1516 - 1005 = 511$ kg is consumed for production of water in reactions (1), (3) and (5)-(7). The resulting amount of water is $511 \times 18/16 = 572$ kg.

Balance for hydrogen. The amount of hydrogen fed into the reactor is $1860 \times 4/30 = 233$ kg. The consumption of hydrogen: formation

of CH_2O—1220 × 2/30 = 81.5 kg, formation of HCOOH—126.5 × × 2/46 = 5.5 kg, formation of CH_4—7.3 × 4/16 = 1.82 kg, formation of H_2O—572 × 2/18 63.6 kg. The amount of hydrogen in the unreacted methanol is 372 × 4/32 = 46.5 kg. The total consumption of hydrogen is 81.5 + 5.5 + 1.82 + 63.6 + 46.5 = = 198.92 kg. The amount of free hydrogen in the mixture of products is 233 — 198.92 = 34.08 kg.

The results are summarized in Table 14.

TABLE 14

Material Balance for the Methanol-oxidation Reactor
(per 1 hour)

INPUTS		OUTPUTS	
Materials	kg	Products	kg
Methanol-air mixture incl.		Formaldehyde	1220
Methanol	1860	Methanol	372
Oxygen	586	Water vapour	572
Nitrogen	1920	HCOOH	126.5
		CO_2	108
		CO	4.3
		CH_4	7.3
		H_2	34.08
		N_2	1920
Total:	4366	*Total:*	4364.18

Further Problems for Students

1. Calculate the consumption of 97% NaCl and 93% H_2SO_4 for production of 1 ton of Na_2SO_4 if the reaction yield is 93%. Find the amount of HCl produced in the process.
2. Calculate the amount of technical-grade calcium carbide containing 85% CaC_2 needed for production of 1000 litres of acetylene if the reaction yield is 0.92.
3. Roasting of 1 ton of limestone produces 168 m^3 of carbon dioxide. The limestone contains 94% $CaCO_3$. Find the degree of dissociation of the limestone and the consumption of limestone per 1000 m^3 of CO_2 under such conditions and 100% yield of the reaction.
4. Find the amount of the flotation concentrate of apatite containing 72% tricalcium phosphate $Ca_3(PO_4)_2$ needed to produce 1 ton of superphosphate fertilizer which contains 19.4% of phosphorus pentoxide. The production losses of P_2O_5 are 2%.

5. Calculate the consumption of pyrite containing 40% S for production of 1 ton of sulphuric acid if the production losses of S and SO_2 amount to 3% and the yield of sulphuric acid from sulphur dioxide is 99%.

6. The gas mixture obtained after thermal oxidation cracking of methane (in production of acetylene) has the following composition (% by volume): C_2H_2—8.5, H_2—57.0, CO—25.3, CO_2—3.7, C_2H_4—0.5, CH_4—4.0, Ar—1.0.

Find the amount of methane that should be processed to obtain 1 ton of methanol from the cracking by-products after separation of acetylene in the reaction

$$CO + 2H_2 \rightleftarrows CH_3OH$$

In practice 1 ton of methane yields 1160 kg of the gas mixture after separation of acetylene.

7. Determine the consumption of ferrous sulphate $FeSO_4 \cdot 7H_2O$ and chromium trioxide CrO_3 for production of 1 ton of iron-chromium catalyst with the composition 90% Fe_2O_3 and 10% Cr_2O_3 used in conversion of carbon monoxide.

8. The gas used in production of calcium hypochlorite contains 8% (by volume) Cl_2 and has the pressure 1.01×10^5 Pa and the temperature 25 °C. The gas leaving the reactor contains 0.25% (by volume) Cl_2. Find the yield of calcium hypochlorite per 100 m^3 of the reacting gas.

9. Calculate the consumption of sodium sulphate containing 95% Na_2SO_4 and that of electrolytical hydrogen containing 97% (by mass) H_2 in production of 1 ton of technical-grade sodium sulphide containing 96% Na_2S:

$$Na_2SO_4 + 4H_2 = Na_2S + 4H_2O$$

The side reactions (yielding NaHS, Na_2SO_3 and $Na_2S_2O_3$) consume 2% of the amounts of sodium sulphate and hydrogen theoretically needed to obtain 1 ton of the commercial-grade product.

10. Calculate the volume of the 65% sulphuric acid (with the 5% excess over the theoretical amount) needed to treat 100 kg of the apatite concentrate containing 38% P_2O_5. The reaction of apatite decomposition can be described by the following equation:

$$2Ca_5F(PO_4)_3 + 7H_2SO_4 = 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF$$

The density of the 65% sulphuric acid is 1.56 g/litre.

11. Calculate the consumption of commercial-grade calcium carbide containing 83% CaC_2 for production of 1 ton of acetylene. The degree of utilization of CaC_2 is 0.88.

12. What is the amount of 20% ammonia water which can be obtained from 1 ton of coal after coking if the coal contains 1% nitrogen and only 1/5 of this nitrogen is reduced to ammonia.

13. Calculate the consumption of materials for production of 1 ton of phosphorus by reducing phosphorite concentrate in the process described by the following overall equation:

$$Ca_3(PO_4)_2+5C+3SiO_2=3CaO\cdot SiO_2+2P+5CO$$

The content of P_2O_5 in the concentrate is 25%; the carbon content of the coke is 94.5% and the reaction yield is 0.85.

14. Calculate the composition of the charge consisting of bauxite, soda, and limestone and used for production of alumina by sintering. Bauxite has the following composition: Al_2O_3—50%, SiO_2—10%, and Fe_2O_3—20%. The limestone contains 90% $CaCO_3$ and the commercial-grade soda contains 96% Na_2CO_3. The sintered mass has the following molar ratios of the components: $Na_2O/(Al_2O_3+Fe_2O_3) = 1$ and $CaO/SiO_2 = 2$. Make the calculations for 100 kg of bauxite.

15. The gas produced by the reaction between the coke and steam contains 6 % (by volume) CO_2. Find the composition of the gas and calculate the material balance for the process per 1 ton of the coke. The coke contains 96.5% (by mass) C and 3.5% (by mass) H_2O. The process is assumed to involve the following reactions:

$$C+H_2O=CO+H_2 \quad \text{(the main reaction)}$$

$$CO+H_2O=CO_2+H_2 \quad \text{(the side reaction)}$$

16. Calculate the material balance (per hour) for the apparatus for catalytic oxidation of sulphur dioxide to sulphur trioxide. The apparatus consumes 10 000 m^3/h of the gas with the following composition (in % by volume): SO_2—8.5, O_2—12.5, N_2—79. The reaction yield is 98%:

$$SO_2+\frac{1}{2}O_2 \rightleftarrows SO_3$$

17. Calculate the material balance (per 1000 m^3 of the product) for chlorine production by electrolysis of the water solution of sodium chloride:

$$2NaCl+2H_2O=2NaOH+Cl_2+H_2$$

The concentration of NaCl in the solution is 310 g/litre; the density of the solution is 1.17 kg/litre. The reaction yield is 50%. The side reactions can be ignored.

18. Calculate the material balance for the plant producing 20 tons of NH_4NO_3 per hour from 47% nitric acid and 100% ammonia gas. The production losses of ammonia and nitric acid amount to 1% of the theoretically needed consumption. The product is obtained in the form of 60% water solution. Find the amount of water evaporated owing to the exothermic reaction

$$HNO_3+NH_3=NH_4NO_3+Q$$

19. Calculate the material balance for the plant producing 3 tons of nitrobenzene per hour in 98% yield. The composition of the nitrating agent (% by mass): HNO_3—20, H_2SO_4—60, H_2O—20. The consumption of the nitrating agent is 4 kg per 1 kg of benzene. The reaction is described by the equation

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O$$

Chapter II

Equilibria of Chemical Technological Processes

Introduction

Chemical interaction between the starting materials, the direct reaction, is accompanied by the chemical interaction between the reaction products, that is, the reverse reaction.

With time the rate of the direct reaction decreases and the rate of the reverse reaction increases. When these rates become equal the state of equilibrium is reached which remains stable under the constant concentrations of the reactants and constant temperature and pressure.

According to the mass action law for the reactions

$$mA + nB \rightleftarrows pC + qD$$

the rate of the direct reaction is

$$u_1 = k_1 [A]^m [B]^n$$

and the rate of the reverse reaction is

$$u_2 = k_2 [C]^p [D]^q$$

At equilibrium we have

$$\frac{[C]^p [D]^q}{[A]^m [B]^n} = \frac{k_1}{k_2} = K$$

or

$$\frac{[A]^m [B]^n}{[C]^p [D]^q} = \frac{k_2}{k_1} = K'' = \frac{1}{K} \qquad \text{(II.1)}$$

where K is the equilibrium constant for a given reaction which varies with temperature. Variation of the equilibrium constant is described by the van't Hoff's equation

$$d (\ln K_p)/dT = q_p/RT^2 \qquad \text{(II.2)}$$

where q_p is the heat effect of the reaction whose dependence on temperature is found from the Kirchhoff's equation.

To find the temperature dependence of the equilibrium constant substitute in Eq. (II.2) $q_p = f(T)$ and integrate the equation obtaining the solution in the form of a power series.

The equilibrium constant can be determined in various forms depending on the form of expression for the concentrations of the reactants. If concentrations are expressed in moles/dm^3 or

kmoles/m³ we have

$$K_C = \frac{[C_C]^p [C_D]^q}{[C_A]^m [C_B]^n} \tag{II.3}$$

If concentrations are expressed in partial pressures (Pa, kN/m²) we have

$$K_p = \frac{[p_C]^p [p_D]^q}{[p_A]^m [p_B]^n} \tag{II.4}$$

If concentrations are expressed in mol. or vol. % we have

$$K_N = \frac{[N_C]^p [N_D]^q}{[N_A]^m [N_B]^n} \tag{II.5}$$

The constants K_C, K_p, and K_N are interrelated:

$$K_C = \frac{K_p}{RT^{\Delta N}} = \frac{K_p}{PV^{\Delta N}} = \frac{K_N}{V^{\Delta N}} \tag{II.6}$$

Here $\Delta N = \nu_1 - \nu_2$, $\nu_1 = q + p$, $\nu_2 = m + n$ and R is the gas constant.

For the ideal gas mixture K_p is independent of the pressure. For the real gases K_p varies with pressure. Experiments have shown that at high pressures the equilibrium constant decreases with increasing pressure. This decrease can be taken into account by introducing a special pressure factor (β) into the temperature dependence of the equilibrium constant. Given in Table 15 are the factors in the equa-

TABLE 15

$\sqrt{K_p}$ Values at Various Temperatures and Factors in Eq. (II.7) at Various Pressures

Pressure		β	I	$\sqrt{K_p}$ at t °C		
Pa	at			450	475	500
10.1×10^6	100	1.256×10^{-4}	−2.113	138	188	249
3.03×10^7	300	1.256×10^{-4}	−2.206	113	148	201
6.06×10^7	600	10.856×10^{-4}	−3.059	77.3	112	154
10.1×10^7	1000	26.833×10^{-4}	−4.473	43	67	—

tion for the temperature dependence of the equilibrium constant for the ammonia synthesis at high pressures.

$$\log K'_p = \log \sqrt{K_p} = -\frac{2074.8}{T} + 2.4943 \log T + \\ + \beta T - 1.8564 \times 10^{-7} T^2 + I \tag{II.7}$$

The equilibrium constants at high pressures can be found proceeding from the volatilities of the components. Deviation from ideality for the real gases under high pressures can be described by the activity coefficient. The activity of a material determines the Gibbs energy of the material going over from the standard state to the equilibrium. The activity coefficient γ is proportional to the volatility f:

$$\gamma = f/P$$

At low pressures volatility may be assumed to be equal to pressure. Volatility characterizes the deviation of the real gas from ideality. Pressure can be replaced by volatility in the ideal-gas equation for the real gas. The activity coefficient for a gas depends also on the compressibility coefficient c:

$$c = PV/RT \quad \text{or} \quad V = c\frac{RT}{P}$$

At the pressures higher than (30-40) $\times 10^4$ Pa the equilibrium constant may be expressed as

$$K_f = K_\gamma P \tag{II.8}$$

The values of K_γ found for synthesis of NH_3 at various pressures are given in Table 16.

TABLE 16

K_γ Values at Various Pressures and Temperatures

Pressure		K_γ at t, °C		
Pa	at	400	450	500
10.1×10^6	100	0.895	0.988	0.992
3.03×10^7	300	—	0.750	0.788
6.06×10^7	600	—	0.573	0.612
10.1×10^7	1000	—	0.443	0.487

The constant K_f is independent of pressure while the constant K_p for the equilibrium mixture of real gases depends on pressure and tends to K_f with decreasing pressure since with decreasing pressure gas approaches ideality.

For the ammonia synthesis reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

the equilibrium constants K_p and K_f can be given by the following equations:

$$K_p = \frac{p^2_{NH_3}}{p_{N_2} p^3_{H_2}} \quad \text{and} \quad K_f = \frac{f^2_{NH_3}}{f_{N_2} f^3_{H_2}} \tag{II.9}$$

The equilibrium constant depends on the stoichiometry of the reaction. For instance, if we assume the reaction

$$\frac{1}{2} N_2 + 1\frac{1}{2} H_2 \rightleftarrows NH_3$$

for ammonia synthesis the equilibrium constant is

$$K'_p = \frac{p_{NH_3}}{p^{\frac{1}{2}}_{N_2} p^{\frac{3}{2}}_{H_2}} = \sqrt{K_p} \tag{II.10}$$

For the dissociation reaction

$$2NH_3 \rightleftarrows N_2 + 3H_2$$

the equilibrium constant is

$$K''_p = \frac{p_{N_2} p^3_{H_2}}{p^2_{NH_3}} = \frac{1}{K_p} \tag{II.11}$$

A reaction can be described by various equations so that the equilibrium constant can have various values for the same equilibrium state. Therefore, when the numerical value of the equilibrium constant is given the relevant reaction equations should be specified.

In chemical technological calculations the equilibrium constant is often found from the isothermal thermodynamic potentials—the Gibbs energy at constant pressure G or at constant volume F. Under the standard conditions (the activity coefficient of the gaseous components $\gamma = 1$) the equations for the reaction isotherm which relate the equilibrium constant to variation of the respective isothermal potential have the following form:

$$\Delta G^\circ = -RT \ln K_p \tag{II.12}$$

$$\Delta F^\circ = -RT \ln K_C \tag{II.13}$$

Equations (II.12) and (II.13) can be used at any temperature. The typically used standard temperature is 25 °C (298 K). The quantities ΔG° and ΔF° are defined as the difference of the isothermal potentials between the products and the starting materials. The values of entropy, heat of formation of chemical compounds and the constants for the standard conditions can be found in the chemical handbooks and textbooks on physical chemistry (see, for instance, V. A. Kireev, *Textbook on Physical Chemistry*, Goskhimizdat, Moscow, 1956, pp. 810-813 (in Russian).

Calculations of the Equilibrium Constants and the Equilibrium Product Yields

Problem 1. Ammonia is synthesized in a column under the pressure of 3.03×10^7 Pa (300 at) at the temperature of 450 °C. The gas leaving the column has the following composition (% by volume): NH_3—17.0, N_2—11.0, H_2—72.0. Calculate the ratio of N_2 and H_2 in the gas fed into the column.

Solution. The data on ammonia synthesis are given in the Introduction to this chapter. Ammonia is synthesized in the reaction

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

The equilibrium mixture of products contains 17% NH_3, that is, 1 mole of the mixture contains 0.17 mole of ammonia. According to the reaction equation to produce 0.17 mole of NH_3 the consumption of materials is $0.17/2 = 0.085$ mole of N_2 and $3 \times 0.17/2 = 0.225$ mole of H_2.

The gas fed into the column contains $0.11 + 0.17/2 = 0.195$ mole of N_2 and $0.72 + 3 \times 0.17/2 = 0.975$ mole of H_2. The total is 1.17 moles. Hence, the gas contains $0.195 \times 100/1.17 = 16.7\%$ (by volume) of N_2 and $0.975 \times 100/1.17 = 83.3\%$ (by volume) of H_2. That is, the ratio of N_2 to H_2 in the gas is $16.7 : 83.3 = 1 : 5$.

Problem 2. In synthesis of hydrogen chloride hydrogen is fed in 10% excess of the stoichiometric amount and the mixture of products contains 80% HCl. Calculate the value of K_C for these conditions.

Solution. Hydrogen chloride is synthesized from chlorine and hydrogen produced by electrolysis of the water solution of NaCl. Hydrogen enters into the exothermic reaction with chlorine:

$$H_2 + Cl_2 \rightleftarrows 2HCl + 184.2 \text{ kJ}$$

The reaction is conducted at 2300-2400 °C at a 5-10% excess of hydrogen providing for the safety of the process and for complete utilization of chlorine.

According to the conditions of the process 1.1 moles of hydrogen are taken for 1 mole of chlorine. Since the process occurs without variation of the volume the amount of the mixture at equilibrium is 2.1 moles. The equilibrium mixture has the following composition (moles): HCl—$2.1 \times 0.8 = 1.68$, Cl_2—$1 - 1.68/2 = 0.16$, H_2—$1.1 - 1.68/2 = 0.26$. Hence, we find

$$K_C = \frac{[HCl]^2}{[H_2]\,[Cl_2]} = \frac{(1.68/2.1)^2}{(0.16/2.1)\,(0.26/2.1)} \approx 67.6$$

Problem 3. Find the equilibrium yield of carbon monoxide in gas manufacture by treating coal with steam at $t_1 = 500$ °C and $t_2 =$

$= 700$ °C if $\log (p_{H_2O}/p_{CO}p_{H_2})$ is 1.67 and —0.13, respectively. The pressure is 10.1×10^4 Pa (1 at).

Solution. Manufacture of gas from coal (or any solid fuel) is a high-temperature heterogeneous process in which the organic components of the coal are converted into combustible gases by incomplete oxidation with oxygen or steam (see Chapter 1, Problem 15). Gasification of coal with steam can be described by the following equation:

$$C + H_2O \rightleftarrows CO + H_2$$

Denote the equilibrium content of carbon monoxide in the mixture by X_e. The equilibrium constant is

$$K_p = \frac{p_{CO}p_{H_2}}{p_{H_2O}} = \frac{X_e^2}{1-2X_e}$$

At 500 °C we have

$$\log K_p' = 1.67, \quad K_p' = 46.7, \quad K_p = 1/46.7 = 0.0214$$

Hence, $X_e^2/(1 - 2X_e) = 0.0214$, $X_e^2 + 0.0428X_e - 0.0214 = 0$, $X_e^{500} = 0.12$. At 700 °C we have

$$\log K_p' = -0.13, \quad K_p' = 0.74, \quad K_p = 1/0.74 = 1.35$$

Hence, $X_e^2 + 2.7X_e - 1.35 = 0$ and $X_e^{700} = 0.42$.

Problem 4. Determine the equilibrium constant for the reaction of propylene hydration to propane at 327 °C:

$$C_3H_6 + H_2 \rightleftarrows C_3H_8$$

Solution. If ΔH° is the variation of enthalpy for the standard reaction under the pressure $P = 1.01 \times 10^5$ Pa and at the absolute zero temperature we can write

$$\Delta G^\circ = \Delta G^\circ - \Delta H_0^\circ + \Delta H_0^\circ$$

or

$$\frac{\Delta G^\circ}{T} = \Delta\left(\frac{G^\circ - H_0^\circ}{T}\right) + \frac{\Delta H_0^\circ}{T}$$

The above equation shows that to find the equilibrium constant we should know the value of $(G^\circ - H_0^\circ)/T$ for all the reactants and the heat effect of the reaction at the absolute zero temperature ΔH_0°.

The values of $(G^\circ - H_0^\circ)/T$ can be found from the spectroscopic data and the values of ΔH_0° from the calorimetric results. Moreover, there are equations for calculation of these values and tables have been compiled for them.

Using the tabular values of the standard heats of formation of the compounds we can find from the Hess equation

$$\Delta H_0^\circ = (\Delta H_0^\circ)_{C_3H_8} - [(\Delta H_0^\circ)_{C_3H_6} + (\Delta H_0^\circ)_{H_2}] =$$
$$= -81\,600 - (35\,100 + 0) = -116\,700 \text{ kJ}$$

At 600 K we have

$$\Delta\left(\frac{G^\circ - H_0^\circ}{T}\right) = \left(\frac{G^\circ - H_0^\circ}{T}\right)_{C_3H_8} - \left[\left(\frac{G^\circ - H_0^\circ}{T}\right)_{C_3H_6} + \left(\frac{G^\circ - H_0^\circ}{T}\right)_{H_2}\right] =$$

$$= -264 - [(-266) + (-122)] = 124$$

$$R \ln K_p = -\left[124 + \frac{-11\,6700}{600}\right)\Big] = 72$$

$$\log K_p = +72/2.3 \times 8.31 = 3.787$$

The experimental value of $\log K_p = 3.79$, which agrees with the predicted value $K_p = 6160 = 6.16 \times 10^3$.

Problem 5. Calculate the equilibrium yields of ammonia for ammonia synthesis and the equilibrium constants $K_p' = p_{H_2}^{3/2} p_{N_2}^{1/2} / p_{NH_3}$ at the temperatures $t_1 = 600$ °C and $t_2 = 500$ °C. The process is carried out under the pressure $P = 3.03 \times 10^7$ Pa (300 at); the reactants are taken in the stoichiometric ratio.

Find the variation of the equilibrium yield X_e of ammonia at 500 °C with a decrease of pressure from $P_1 = 300 \times 10^5$ Pa (300 at) to $P_2 = 100 \times 10^5$ Pa (100 at).

Solution. The reaction of ammonia synthesis may be described by the following equations:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

or

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftarrows NH_3$$

The partial pressures of the components in the equilibrium mixture at the temperature T and the pressure P are

$$p_{NH_3} = \frac{X_e}{100} P$$

$$p_{N_2} = \frac{1}{4} \frac{(100 - X_e)}{100} P$$

$$p_{H_2} = \frac{3}{4} \frac{(100 - X_e)}{100} P$$

where X_e is the equilibrium content of NH_3 in the mixture.

Substituting the partial pressures in the equation for K_p we obtain

$$K_p = \frac{100 \sqrt{\left[\frac{3}{4}(100 - X_e) P\right]^3 \frac{1}{4}(100 - X_e) P}}{X_e P \sqrt{100^3 \times 100}} = \frac{P (100 - X_e)^2 \, 0.325}{X_e \cdot 100}$$

$$\frac{(100 - X_e)^2}{X_e} = \frac{K_p}{0.00325P}$$

Designating $K_p/0.00325P = A$ we obtain the quadratic equation

$$X_e^2 - (200 + A) X_e - 100^2 = 0$$

which yields

$$X_e = \frac{200 + A \pm \sqrt{(200 + A)^2 - 4 \times 10^4}}{2}$$

Using Eq. (II.7) and the appropriate values of β and I from Table 15 we can find log K_p for $T_1 = 873$ K and $P_1 = 300 \times 10^5$ Pa (300 at):

$$\log K_p = -2077/873 + 2.4943 \log 873 + 1.256 \times 10^{-4} \times 873 - \\ - 1.8564 \times 10^{-7} \times 873^2 + (-2.206) = 2.721$$

Hence,

$$K_p = 526 \times 10^5 \text{ Pa (526 at)}$$
$$A = 526 \times 10^5/300 \times 10^5 \times 0.00325 = 535$$
$$X_e = (200 + 535 \pm \sqrt{535^2 - 4 \times 10^4})/2$$

Thus, the equilibrium concentration of NH_3 is $X_e = 13.9\%$, the equilibrium concentration of N_2 is $(100 - 13.9)/4 = 21.53\%$, and the equilibrium concentration of H_2 is $3\ (100 - 13.9)/4 = 64.75\%$.

In a similar way, we find for $T_2 = 773$ K and $P = 300 \times 10^5$ Pa (300 at): $K_p = 200$; $A = 200/300 \times 0.00325 = 205$;

$$X_e = \frac{200 + 205 \pm \sqrt{405^2 - 4 \times 10^4}}{2} = 19.1\% \text{ NH}_3$$

and the equilibrium concentrations of N_2 is $80.9/4 = 20.23\%$ and of H_2 $80.9 \times 3/4 = 60.67\%$.

Under the pressure $P_2 = 100 \times 10^5$ Pa (100 at) and $T = 873$ K we have $\beta = 0$ and $I = 1.993$* so that

$$\log K_p = -2074.8/773 + 2.4943 \log 773 - 1.8564 \times 10^{-7} \times \\ \times 773^2 - 1.993 = 2.406$$
$$K_p = 225 \times 10^5 \text{ Pa (255 at)}$$
$$A = 255 \times 10^5/100 \times 10^5 \times 0.00325 = 7846$$
$$X_e = (255 + 7846 \pm \sqrt{8101^2 - 4 \times 10^4})/2 = 1.5\% \text{ NH}_3,$$
$$98.5/4 = 24.6\% \text{ N}_2,\ 98.5 \times 3/4 = 73.9\% \text{ H}_2$$

Calculations of the Composition of Reaction Mixtures and Material Balances for Industrial Processes Based on Reversible Reactions

Problem 6. Direct hydration of ethylene over the phosphorus catalyst (in manufacture of ethanol) at 300 °C and under the pressure of 80×10^5 Pa (80 at) converts 10% (by volume) of ethylene into

* See *Handbook of Nitrogen Processes*, vol. 1, Khimiya, Moscow, 1967, p. 368 (in Russian).

ethanol. Find the composition of the final reaction mixture and the equilibrium constant ignoring the side reactions.

Solution. The reaction is described by the equation

$$CH_2=CH_2+H_2O \rightleftarrows C_2H_5OH$$

according to which 1 mole of the starting mixture contains 0.5 mole of each of the reactants. At the end of the reaction $0.5 \times 0.1 = 0.05$ mole of each of the reactants has reacted giving rise to 0.05 mole of ethanol. The final gas mixture contains $0.5 - 0.05 = 0.45$ mole of ethylene and steam each. The amount of the final reaction mixture per 1 mole of the starting gas is $0.45 + 0.45 + 0.05 = 0.95$ mole. The mixture has the following composition (in % by volume): ethylene—$0.45 \times 100/0.95 = 47.4$, steam—47.4, ethanol—5.2 (total—100).

The equilibrium constant is

$$K_p = p_{C_2H_5OH}/p_{C_2H_4}p_{H_2O} = 0.052 \times 80 \times 10^5/0.474^2 \times 80^2 \times 10^{10} =$$

$$= 2.9 \times 10^{-8} \text{ Pa } (2.9 \times 10^{-3} \text{ at})$$

There is another approach to solving this problem.

For the reaction $A + B \rightleftarrows D$ when the reactants are taken in the stoichiometric ratio the equilibrium concentrations in fractions of a mole are

$$[A^*] = (1 - X_e)/2, \quad [B^*] = (1 - X_e)/2, \quad \text{and} \quad [D^*] = X_e$$

Here X_e is the equilibrium yield equal to the concentration of the product D in the final reaction mixture.

The equilibrium constant is

$$K_p = \frac{p_D}{p_A p_B} = \frac{X_e P}{\left(\frac{1-X_e}{2}\right)^2 p^2} = \frac{4X_e}{(1-X_e)^2 P}$$

Since $X_e = 0.052$ we obtain

$$K_p = \frac{4 \times 0.052}{(1-0.052)^2 \times 80 \times 10^5} = 2.9 \times 10^{-8} \text{ Pa } (2.9 \times 10^{-3} \text{ at})$$

Problem 7. The starting mixture for hydrogen chloride oxidation has the following composition (in % by volume): HCl—35.5, air—64.5. The oxidation process is carried out over the chromium oxide catalyst at 370 °C and under the pressure of 10^5 Pa (1 at). The content of Cl_2 in the final reaction mixture is 13.2%. Calculate the equilibrium composition of the reaction mixture and the equilibrium constant

$$K_p = \frac{p^2_{Cl_2} p^2_{H_2O}}{p^4_{HCl} p_{O_2}}$$

Solution. Catalytic oxidation of hydrogen chloride is a process of utilization of the waste gases produced in chlorination of organic compounds. Oxidation of HCl yields chlorine which is a valuable raw material for many organic syntheses. The reaction can be described by the following equation:

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

The composition of the starting gas is as follows (in % by volume): HCl—35.5, O_2—64.5 × 0.21 = 13.5, N_2—64.5 × 0.79 = 51.0.

At equilibrium 1 mole of the final reaction mixture has the following composition: Cl_2—0.132 mole, H_2O—0.132 mole, HCl + + O_2 + N_2—1 — 0.264 = 0.736 mole.

The process occurs with a decrease in volume. The amount of the starting gas required to produce 1 mole of the equilibrium reaction mixture contains 0.736 mole due to HCl, O_2 and N_2 and the amounts of HCl and O_2 needed to produce 0.132 mole of Cl_2 and 0.132 mole of H_2O, that is, 0.264 mole of HCl and 0.264/4 = 0.066 mole of O_2. That is, 0.330 mole. Hence, the amount of the starting gas per 1 mole of the reaction mixture is 0.736 + 0.330 = 1.066 moles, including 1.066 × 0.355 = 0.379 mole of HCl, 1.066 × 0.135 = 0.144 mole of O_2 and 1.066 × 0.510 = 0.543 mole of N_2.

At equilibrium 1 mole of the reaction mixture contains 0.379 — — 0.264 = 0.115 mole of HCl, 0.144 — 0.066 = 0.078 mole of O_2, 0.543 mole of N_2, 0.132 mole of Cl_2 and 0.132 mole of H_2O.

At equilibrium the components of the reaction mixture have the following partial pressures: $p_{H_2O} = p_{Cl_2} = 0.132 \times 10^5$ Pa (0.132 at), $p_{O_2} = 0.078 \times 10^5$ Pa (0.078 at), $p_{HCl} = 0.115 \times$ $\times 10^5$ Pa (0.115 at).

The equilibrium constant is

$$K_p = p_{Cl_2}^2 p_{H_2O}^2 / p_{HCl}^4 p_{O_2} = 10^{10} \times 0.132^2 \times 0.132^2 \times 10^{10}/10^{20} \times$$
$$\times 0.115^4 \times 0.078 \times 10^5 = 22.4 \times 10^5 \text{ Pa (22.4 at)}$$

Problem 8. The mixture of products after one-step conversion of methane has the following composition (in % by volume): H_2—52, CO—21, CO_2—7.5, N_2—19, CH_4—0.5. The gas mixture is passed through humidifier and heat exchanger and fed into the apparatus for conversion of carbon monoxide.

Calculate the amount of steam needed for the process (per 100 m^3 of gas) if the content of CO in the waste gas is not more than 3.5% (by volume). Calculate also the equilibrium yield of the process. The process is carried out at 500 °C under the pressure of 1.01 × $\times 10^5$ Pa.

Solution. In production of synthetic ammonia conversion of CO with steam is the second stage in preparation of the nitrogen-hydrogen mixture since conversion of the natural-gas methane (the first

stage) yields the gas mixture containing about 20% of CO. Conversion of CO may also be used as an independent process for production of nitrogen-hydrogen mixture from the water or semi-water producer gas. Conversion of carbon monoxide can be described by the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The equilibrium constant at 500 °C can be found from the equation

$$\log K_p = -2059/T + 1.5904 \log T - 1.817 \times 10^{-3}T + \\ + 5.65 \times 10^{-7}T^2 - 8.24 \times 10^{-11}T^3 - 1.5313$$

Hence, $K_p = 0.180$ at $T = 773$ K.

Write down the compositions of the starting gas and the reaction mixture denoting the amount of unreacted CO as X:

	Starting gas	Reaction mixture
CO	21.0	X
CO_2	7.5	$7.5+(21-X)$
H_2	52.0	$52+(21-X)$
N_2	19.0	19.0
CH_4	0.5	0.5
	$V=100$ m³	$V=(121-X)$ m³

The CO content in the dry reaction mixture should be not more than 3.5%. If it is 3.5% we have $X = (121 - X) \times 3.5/100$ or $X = 4.1$ m³. Hence, the volume of the dry converted gas per 100 m³ of the initial gas is $121 - 4.1 = 116.9$ m³ including 4.1 m³ of CO, 24.4 m³ of CO_2, 68.9 m³ of H_2, 19.0 m³ of N_2, and 0.5 m³ of CH_4.

Denote the amount of steam required for the reaction as Y. Then at equilibrium the amount of H_2O is $Y - (21 - X) = Y - (21 - 4.1) = Y - 16.9$.

Since for this reaction $K_p = K_C = K_N$ any volume concentration can be substituted in the equation for the equilibrium constant:

$$K_p = 0.180 = \frac{[CO]\,[H_2O]}{[CO_2]\,[H_2]} = \frac{4.1\,(Y-16.9)}{24.4 \times 68.9}$$

Hence, $Y = 91$ m³. The equilibrium yield of the reaction is $X_e = \frac{21-4.1}{21} \times 100 = 80\%$.

Problem 9. For the process of conversion of carbon monoxide with steam the equilibrium constant is

$$K_C = \frac{[CO_2]\,[H_2]}{[CO]\,[H_2O]} = 1$$

Determine the equilibrium composition of the reaction mixture if 2 moles of steam are taken for each mole of carbon monoxide.

Solution. The conversion process is described by the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The equilibrium concentration of CO_2 in the converted gas is denoted by X_e. Then the reaction mixture has the following composition: CO—$1 - X_e$, H_2O—$2 - X_e$, CO_2—X_e, H_2—X_e. Substitute these concentrations in the equation for the equilibrium constant:

$$K_C = \frac{X_e^2}{(1 - X_e)(2 - X_e)} = 1$$

Hence, $X_e = 2/3$; the equilibrium concentrations of the components are (in molar fractions): CO—1/3, H_2O—4/3, CO_2—2/3, and H_2—2/3.

Problem 10. Oxidation of nitrogen oxide to nitrogen dioxide is accompanied by formation of the dimer N_2O_4:

$$2NO_2 \rightleftarrows N_2O_4$$

Calculate the degree of dimerization of NO_2 for the starting mixture containing 5% (by volume) of NO_2 under the pressure of 10^5 Pa and at 40 °C. The equilibrium constant is $K'_p = p^2_{NO_2}/p_{N_2O_4} = 0.435$.

Solution. Oxidation of NO to NO_2 and partial dimerization of NO_2 occur in manufacture of nitric acid from the nitrogen gases produced by oxidation of ammonia. The process is carried out at low temperatures and atmospheric or elevated (up to 10^6 Pa) pressures.

For 100 m^3 of the starting gas mixture containing 5% of NO_2 the change in the volume owing to dimerization can be found in the following way:

$$\begin{array}{ccc} 2NO_2 & \rightleftarrows & N_2O_4 \\ 5-2X & & X \end{array}$$

$$V_{equil} = 100 + X - 2X = 100 - X$$

In this case ($P = 10^5$ Pa) the molar fractions are equal to the partial pressures of the monomer and the dimer at equilibrium: NO_2—$(5 - 2X)/(100 - X)$ and N_2O_4—$X/(100 - X)$. Hence, we can write $K_p = 0.435 = (5 - 2X)^2 (100 - X)/X (100 - X)^2 = (5 - 2X)^2/X (100 - X)$. We find $X = 0.413$ and $2X = 0.826$.

The yield of the dimer is $0.826 \times 100/5 = 16.5\%$.

Problem 11. In manufacture of sulphuric acid using the contact process sulphur dioxide is oxidized to sulphur trioxide. The starting gas has the following composition (in % by volume): SO_2—11, O_2—10, N_2—79. Oxidation is carried out at 570 °C under the pressure of 1.2×10^5 Pa. The degree of oxidation is 70%.

Calculate the composition of the reaction mixture and the equilibrium constant $K'_p = \sqrt{K_p} = p_{SO_3}/p_{SO_2} p^{0.5}_{O_2}$.

Solution. The reaction per 1 mole of the product is described by the following equation:

$$SO_2 + 0.5O_2 \rightleftarrows SO_3$$

At equilibrium the reaction mixture has the following composition (per 1 mole): SO_3—$0.11 \times 0.7 = 0.0770$, SO_2—$0.11 \times 0.3 = 0.0330$, O_2—$0.10 - 0.077/2 = 0.0615$, N_2—0.7900 (total—0.9615)

Thus, oxidation of 1 mole of the gas decreases its volume to 0.9615 mole and the mixture has the following equilibrium composition (in molar fractions): SO_3—$0.0770/0.9615 = 0.0797$, SO_2—$0.0330/0.9615 = 0.0342$, O_2—$0.0615/0.9615 = 0.0638$, N_2—$0.79/0.9615 = 0.8223$. Hence, the partial pressures of the components of the reaction mixture are: $p_{SO_3} = 1.2 \times 10^5 \times 0.0797 = 0.096 \times 10^5$ Pa, $p_{SO_2} = 1.2 \times 10^5 \times 0.0342 = 0.041 \times 10^5$ Pa, $p_{O_2} = 1.2 \times 10^5 \times 0.0638 = 0.076 \times 10^5$ Pa, $p_{N_2} = 1.2 \times 10^5 \times 0.8223 = 0.987 \times 10^5$ Pa (total—1.2×10^5 Pa).

The equilibrium constant is

$$K'_p = p_{SO_3}/p_{SO_2}p_{O_2}^{0.5} =$$

$$= 0.096 \times 10^5/0.041 \times 10^5 \sqrt{0.076 \times 10^5} = 0.85 \times 10^{-2}$$

Problem 12. In the process of methanol synthesis the equilibrium content of methanol in the reaction mixture is 24.2% (by volume) when the process is carried out at 350 °C under the pressure of 300×10^5 Pa (300 at). The H_2 : CO ratio in the starting mixture is 4 : 1. For the stoichiometric H_2 : CO ratio the equilibrium concentration of methanol in the reaction mixture is 37.8% (by volume).

Calculate the equilibrium composition of the reaction mixture and the equilibrium constants $K_p = p_{CH_3OH}/p_{CO}p_{H_2}^2$.

Solution. The physico-chemical principles and the technology of methanol synthesis from a mixture of CO and H_2 are similar to those of the ammonia synthesis. The mixture of CO and H_2, similar to the nitrogen-hydrogen mixture, is produced by conversion of the producer or natural gas. The reaction of methanol synthesis, like the reaction of ammonia synthesis, necessitates a high activation energy; the reaction is reversible and exothermic and leads to a decrease in volume. The process is carried out at high temperatures and pressures in the presence of the active catalyst. The product yield is low owing to the reversibility of the reaction as well as to the side reactions. The process makes use of the continuous cycle method.

The reaction of methanol synthesis is described by the following equation:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

At equilibrium 1 mole of the reaction mixture contains 0.242 mole of methanol and $1 - 0.242 = 0.758$ mole of CO + H_2. Production of 0.242 mole of methanol consumed 0.242 mole of CO and $0.242 \times 2 = 0.484$ mole of hydrogen, that is, 0.726 mole in total. The amount of the starting gas per 1 mole of the reaction mixture is $0.758 + 0.726 = 1.484$ mole, including $1.484 \times 1/5 = 0.297$ mole

of CO and $1.484 \times 4/5 = 1.187$ mole of H_2. At equilibrium 1 mole of the reaction mixture contains 0.242 mole of methanol, $0.297 - 0.242 = 0.055$ mole of CO and $1.187 - 0.484 = 0.703$ mole of hydrogen.

The components of the mixture have the following partial pressures: $p_{CH_3OH} = 0.242 \times 300 \times 10^5$ Pa, $p_{CO} = 0.055 \times 300 \times 10^5$ Pa, $p_{H_2} = 0.703 \times 300 \times 10^5$ Pa. Hence, the equilibrium constant is

$$K_p = 0.242 \times 300 \times 10^5 / 0.055 \times 300 \times 10^5 \times 0.703^2 \times 300^2 \times 10^{10} = 0.98 \times 10^{-14}$$

The stoichiometric H_2 : CO ratio for methanol synthesis reaction is 2 : 1. Then, the methanol content in the reaction mixture is 0.378 and the content of hydrogen and CO is $1 - 0.378 = 0.622$.

Production of 1 mole of methanol consumes 0.378 mole of CO and 0.756 mole of hydrogen.

At equilibrium the reaction mixture has the following composition (in molar fractions): CH_3OH—0.378, CO—$0.585 - 0.378 = 0.207$, H_2—$1.170 - 0.756 = 0.414$. Using the partial pressures we can find the equilibrium constant:

$$K_p = 0.378 \times 300 \times 10^5 / 0.207 \times 300 \times 10^5 \times 0.414^2 \times 300^2 \times 10^{10} = 1.18 \times 10^{-14}$$

Problem 13. The starting mixture for oxidation of hydrogen chloride has the following composition (in % by volume): O_2—32.4, HCl—67.6 (see Chapter II, Problem 7). The process occurs at 386 °C and under the pressure of 10^5 Pa. The equilibrium reaction mixture contains 31.4% Cl_2.

Calculate the equilibrium composition of the reaction mixture and the equilibrium constant $K_p = p^4_{HCl} p_{O_2} / p^2_{Cl_2} p^2_{H_2O}$.

Solution. Oxidation of hydrogen chloride may be described by the following equation:

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O$$

The equilibrium reaction mixture contains 31.4% (by volume) Cl_2. Hence, 1 mole of the equilibrium reaction mixture contains 0.314 mole of Cl_2, 0.314 mole of H_2O and $1 - 0.314 \times 2 = 0.372$ mole of HCl + O_2.

Production of 0.314 mole of H_2O and 0.314 mole of Cl_2 consumes $0.628/4 = 0.157$ mole of O_2 and 0.628 mole of HCl, that is, 0.785 mole of the reactants. The total amount of reactants per 1 mole of products is $0.372 + 0.785 = 1.157$ moles, including $1.157 \times 0.324 = 0.375$ mole of O_2 and $1.157 \times 0.676 = 0.782$ mole of HCl.

At equilibrium 1 mole of the reaction mixture contains $0.375 - 0.157 = 0.218$ mole of O_2 and $0.782 - 0.628 = 0.154$ mole

of HCl. Hence, the equilibrium reaction mixture has the following composition (in % by volume): Cl_2—31.4, H_2O—31.4, HCl—15.4, O_2—21.8.

The components of the reaction mixture have the following partial pressures: $p_{O_2} = 0.218 \times 10^5$ Pa, $p_{HCl} = 0.154 \times 10^5$ Pa, $p_{Cl_2} = p_{H_2O} = 0.314 \times 10^5$ Pa. Hence,

$$K_p = 0.154^4 \times 0.218 \times 10^{20} \times 10^5 / 0.314^2 \times 0.314^2 \times 10^{10} \times 10^{10} = 1.2 \times 10^3 \text{ Pa}$$

Problem 14.* Calculate the material balance for conversion of the natural-gas methane. The plant consumes 4700 m^3 of the natural gas per hour. The natural gas has the following composition (in % by volume): CH_4—97.8, C_2H_6—0.5, C_3H_8—0.2, C_4H_{10}—0.1, N_2—1.4. The steam-gas ratio in the starting mixture is 2.5. The degree of conversion of hydrocarbons is 67%.

The process involves the following reactions:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 - 38.9 \text{ kJ/mole} \quad (1)$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 - 248.3 \text{ kJ/mole} \quad (2)$$

$$CH_4 + 0.5O_2 \rightleftarrows CO + 2H_2 + 34.8 \text{ kJ/mole} \quad (3)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 41.0 \text{ kJ/mole} \quad (4)$$

The ratio CO : CO_2 in the converted gas can be taken to be that at the equilibrium of the reaction (4) at the temperature of the gas leaving the converter, that is, at 700 °C since, first, this reaction reaches its equilibrium faster than the reactions (1)-(3) and, secondly, at this temperature the equilibria of other reactions are more considerably shifted towards the reaction products.

These reactions have the following approximate values of the equilibrium constants K_p at 700 °C: (1)—25, (2)—20, (3)—3×10^{11}, (4)—1.54.

Calculations should be made for 100 m^3 of the natural gas and then expressed in terms of kg/h.

Solution. Conversion of the natural-gas methane is the process for production of hydrogen and nitrogen-hydrogen mixture for ammonia synthesis. The reactions (1)-(4) between the natural-gas methane and steam, CO_2, and oxygen are, typically, carried out in catalytic tubular or shaft converters. The reactions (1) and (2) are endothermic and the process as a whole consumes energy which is supplied by burning a part of the natural gas to CO_2 and H_2O and by the reactions (3) and (4) which are exothermic. The higher hydrocarbons found in the natural gas (C_2H_6, C_3H_8, and C_4H_{10}) are also converted to CO and H_2.

* M. E. Pozin *et al. Calculations of the Technology of Inorganic Compounds*, Khimiya, Leningrad, 1966, p. 480 (in Russian).

Denote the content of components in the converted gas (in m^3) as V_{CO_2}, V_{CO} and V_{H_2} and the amount of steam (in m^3) reacted with hydrocarbons as V_{H_2O}.

The volume of unreacted hydrocarbons in the converted gas (calculated as CH_4) is $(97.8 + 0.5 \times 2 + 0.2 \times 3 + 0.1 \times 4)(100 - 67)/100 = 32.9$ m^3. To determine the composition of the converted gas we shall write down the material balances (per 100 m^3) for each element.

(1) The material balance for carbon*:

$$97.8 + 2 \times 0.5 + 3 \times 0.2 + 4 \times 0.1 = V_{CO_2} + V_{CO} + 32.9$$

Hence,

$$V_{CO_2} = 66.9 - V_{CO} \qquad (a)$$

(2) The material balance for oxygen (allowing for the fact that the starting steam-gas mixture contains $100 \times 2.5 = 250$ m^3 of steam):

$$0.5 \times 250 = V_{CO_2} + 0.5V_{CO} + 0.5(250 - V_{H_2O})$$

Hence

$$V_{CO_2} + 0.5V_{CO} - 0.5V_{H_2O} = 0 \qquad (b)$$

(3) The material balance for hydrogen:

$$2 \times 97.8 + 3 \times 0.5 + 4 \times 0.2 + 5 \times 0.1 + 250 = V_{H_2} + 2 \times 32.9 + (250 - V_{H_2O})$$

Hence,

$$V_{H_2} = V_{H_2O} + 132.6 \qquad (c)$$

Since the $CO : CO_2$ ratio in the product mixture is determined by the equilibrium of the reaction (4) at 700 °C the equilibrium constant is

$$K_p = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}} = \frac{V_{CO_2} V_{H_2}}{V_{CO} V_{H_2O}} = 1.54 \qquad (d)$$

(Here $K_p = K_C = K_N$ and the equilibrium constant can be expressed in terms of the volumes of the components for the volume of the converted gas produced from 100 m^3 of the natural gas.)

Find the volumes of the components in terms of V_{H_2O} from equations (a), (b), and (c) and substitute them in equation (d).

Equations (a) and (b) yield

$$V_{CO} = 133.8 - V_{H_2O} \qquad (e)$$

* In equation (a) the factors 2, 3, and 4 mean that 1 mole of C_2H_6 gives rise to 2 moles of CO or CO_2, 1 mole of C_3H_8 gives rise to 3 moles of CO or CO_2, and so on, in equation (b) the factor 0.5 means that 1 mole of H_2O and 1 mole of CO contain 0.5 mole of O_2, in equation (c) the factors 2, 3, 4 and 5 mean that 1 mole of CH_4 gives rise to 2 moles of H_2, and so on.

Equations (a) and (e) yield

$$V_{CO_2} = V_{H_2O} - 66.9 \qquad (f)$$

Substituting in equation (d) equations (c), (e), and (f) we obtain

$$K_p = \frac{(V_{H_2O} - 66.9)(V_{H_2O} + 132.6)}{(133.8 - V_{H_2O})(250 - V_{H_2O})} = 1.54 \qquad (g)$$

Equation (g) yields

$$V^2_{H_2O} - 66.9V_{H_2O} + 132.6V_{H_2O} - 8871 = 51\,500 - 385V_{H_2O} -$$
$$- 206V_{H_2O} + 1.54V^2_{H_2O}, \quad V^2_{H_2O} - 1216V_{H_2O} + 11\,1800 = 0$$

$$V_{H_2O} = 1216/2 \pm \sqrt{(1216/2)^2 - 11\,1800} = 608 \pm 508$$
$$V_{H_2O} = 100 \text{ m}^3$$

For the other components we obtain: $V_{CO_2} = 100 - 66.9 = 33.1$ m³, $V_{CO} = 133.8 - 100 = 33.8$ m³, and $V_{H_2} = 100 + 132.6 = 232.6$ m³. The amount of steam remaining in the converted gas is $250 - 100 = 150$ m³.

Table 17 presents the data on the composition of the converted gas.

TABLE 17

The Composition of the Converted Gas

Component	Wet gas		Dry gas	
	m³	% by volume	m³	% by volume
CH_4	32.9	6.8	32.9	9.90
H_2	232.6	48.07	232.6	69.60
CO	33.8	7.0	33.8	10.15
CO_2	33.1	6.84	33.1	9.93
N_2	1.4	0.29	1.4	0.42
H_2O	150.0	31.0	—	—
Total:	483.8	100.0	333.8	100.0

These data can be used to calculate the material balance for methane conversion (Table 18).

Owing to the inaccuracy of calculations the balance shows a discrepancy of 3.2 kg, that is, about 0.02%.

TABLE 18

The Material Balance for Methane Conversion

INPUTS			OUTPUTS		
Materials	kg	m³	Products	kg	m³
Natural gas:			Dry converted gas:		
CH_4	3290.00	4596.60	CH_4	1104.50	1546.3
C_2H_6	31.50	23.50	H_2	977.60	10932.2
C_3H_8	18.30	9.40	CO	1992.80	1588.6
C_4H_{10}	12.20	4.70	CO_2	3057.40	1555.7
N_2	82.20	65.80	N_2	82.20	65.8
Steam	3434.20	4700.00	Steam	7214.50	15688.6
	9447.0	11750.0		5663.50	7050.0
Total:	12881.2	16450.0	*Total*:	12878.00	22738.6

Further Problems for Students

1. At 527 °C and under the pressure of 1.01×10^5 Pa the equilibrium degree of dissociation of carbonyl chloride is 0.75. Find the equilibrium constants K_p and K_C for this reaction.
2. A 6-litre laboratory reaction vessel contains 9.2 g of N_2O_4 at the temperature of 111 °C and under the pressure of 10^5 Pa. Determine the equilibrium constant K_p for the reaction

$$N_2O_4 \rightleftarrows 2NO_2$$

3. The reaction between carbon dioxide and carbon (metallurgical process, gasification of solid fuel) at 1000 °C and under the pressure of 30×10^5 Pa gives rise to the equilibrium product mixture containing 17% (by volume) of CO_2. Determine the CO_2 content in the equilibrium product mixture at 20×10^5 Pa.
4. Conversion of carbon monoxide with steam according to the equation

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 36.6 \text{ kJ}$$

is carried out at 500 °C. Determine the composition of the equilibrium reaction mixture (in % by volume) if the starting molar ratio steam-carbon monoxide was 2 : 1 and $K_p = 1$.
5. The gas mixture containing 20 % (by volume) CO and 80 % (by volume) N_2 is passed over FeO at 1000 °C and under the pressure

of 10^5 Pa. The reaction can be described by equation

$$FeO + CO \rightleftarrows Fe + CO_2$$

Find the yield of iron (kg) per 1000 m^3 of the gas and the composition of the equilibrium reaction mixture if $K_C = 0.403$.

6. The dry semi-water gas has the following composition (in % by volume): CO—37, H_2—35, N_2—22, CO_2—6. The gas is converted at 500 °C. Find the steam-gas ratio providing for the equilibrium degree of conversion 0.51 and determine the composition of the converted gas (in % by volume). The equilibrium constant for the reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ has the following temperature dependence:

$$\log K_p = -2059/T + 1.5 \log T - 1.82 \times 10^{-3} T + 5.65 \times 10^{-7} T^2 - 8.2 \times 10^{-11} T^3 - 1.53$$

7. Determine the yield of NO for its synthesis from the air at 2400 °C if it amounts to 80% of the equilibrium yield and $K_p = K_C = K_N = [NO]^2/[N_2]\,[O_2] = 0.0035$.

8. Determine the yield of hydrogen in the reaction

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$

if the equilibrium reaction mixture contains 40.7% (by volume) of steam.

9. Find the equilibrium yield of products for steam conversion of carbon monoxide if the starting steam-carbon monoxide ratio is (1) stoichiometric and (2) 3 : 1 (by volume). The equilibrium constant $K = 0.15$.

10. Calculate the equilibrium composition of the reaction mixture for methanol synthesis when the starting H_2 : CO ratio is 4.5, the content of the neutral components is 13.8%, the pressure is 300 × × 10^5 Pa (300 at) and the temperature is 365 °C. The temperature dependence of the equilibrium constant $K_p = p_{CH_3OH}/p_{CO}p^2_{H_2}$ is

$$\log K_p = 3925/T - 9.84 \log T - 0.00347T + 14.8$$

11. Calculate the equilibrium yield of ammonia (the ammonia content in the equilibrium reaction mixture) for ammonia synthesis from the nitrogen-hydrogen mixture with the exact stoichiometric composition at 580 °C and under 300 × 10^5 Pa (300 at). The temperature dependence of the equilibrium constant is $\log K_p = -2074.8/T + 2.4943 \log T + 1.256 \times 10^{-4} T - 1.8564 \times \times 10^{-7} T^2 - 2.206$.

Chapter III

The Basic Principles for Drawing up Energy (Heat) Balances and Heat Calculations for Chemical Technological Processes

Introduction

The energy (heat) balance for any apparatus can be described by the equation relating inputs and outputs of energy (heat) of the process (apparatus). The energy balance is based on the law of conservation of energy according to which in a closed system the sum of the energies of all types is constant. The chemical technological processes are, typically, described by the heat balance equation

$$\sum Q_{\text{input}} = \sum Q_{\text{output}} \qquad \text{(III.1)}$$

or

$$\sum Q_{\text{input}} - \sum Q_{\text{output}} = 0 \qquad \text{(III.2)}$$

In terms of the heat balance the law of conservation of energy means that the inputs of heat in an apparatus or a process should be equal to the consumption of heat in this apparatus or process.

For the continuous-operation apparatus or process the heat balance is, typically, written for unit time and for batch-operated apparatus or process the balance is written for the cycle period or the individual stage time of the process.

The heat balance is calculated from the material balance taking into account the thermal effects (exothermic and endothermic) of the chemical reactions and the physical transformations (evaporation, condensation, etc.) occurring in the apparatus and the input of heat from the outside and removal of heat with the reaction products and through the walls of the apparatus.

The heat balance, like the material one, is written down in the form of tables and diagrams and the calculations are made with the following equation:

$$Q_s + Q_l + Q_g + Q_{ph} + Q_r + Q_e = Q'_s + Q'_l + Q'_g + Q'_{ph} + Q'_r + Q'_e \qquad \text{(III.3)}$$

Here Q_s, Q_l, and Q_g are the heats supplied to the apparatus by the solid, liquid, and gaseous phases, respectively, Q'_s, Q'_l, and Q'_g are the heats removed from the apparatus with the solid, liquid, and gaseous reaction products and unreacted starting materials: Q_{ph} and Q'_{ph} are the heats liberated and consumed with the physical processes; Q_r and Q'_r are the heats liberated and consumed with the exothermic and endothermic reactions; Q_e is the heat supplied to the apparatus from the external sources (with flue gases, hot air, by combustion of fuel, electric power consumption, etc.), and Q'_e is the loss of heat to the environment or to cooling agents.

The heats Q_s, Q_l, Q_g, Q'_s, Q'_l and Q'_g for each material fed to the apparatus and product discharged from it are given by the formula

$$Q = Gct \tag{III.4}$$

where G is the amount of the material, c is its mean specific heat, and t is the temperature (typically, in centigrade degrees).

The specific heats of gases (in J/kmole K) at a given absolute temperature T are given by the equation*

$$c = a_0 + a_1 T + a_2 T^2 \tag{III.5}$$

Calculations are made usually for mixtures so that in Eq. (III.4) the specific heat c_m of the mixture is used which is found from additivity of the heat effects. For instance, for the mixture of three compounds with the specific heats c_1, c_2 and c_3 taken in the amounts G_1, G_2 and G_3 the specific heat is

$$c_m = \frac{G_1 c_1 + G_2 c_2 + G_3 c_3}{G_1 + G_2 + G_3} \tag{III.6}$$

The total heat of the physical exothermic processes occurring in the apparatus is given by the equation (for the mixture of three components)

$$Q_{ph} = G_1 r_1 + G_2 r_2 + G_3 r_3 \tag{III.7}$$

where G_1, G_2, and G_3 are the amounts of the components which have undergone phase transitions and r_1, r_2, and r_3 are the heats of the phase transitions (condensation, crystallization, dissolving, etc.). The number of terms in the right-hand side of Eq. (III.7) is equal to the number of components undergoing phase transformations in the course of the process. Some physical processes (desorption of gases, evaporation, fusion, dissolving) consume heats Q'_{ph} which are found in the same way.

The heat effects of the chemical reactions can be found from the heats of formation and combustion of the compounds involved in the process. According to the Hess law the heat effect of the reaction is found as the difference between the heats of formation of all the compounds in the right-hand side of the reaction equation and those in the left-hand side of the equation. For instance, for the reaction $A + B = D + F + Q_r$ the isobaric heat effect is

$$Q^0_r = Q^0_{form.\,D} + Q^0_{form.\,F} - (Q^0_{form.\,A} + Q^0_{form.\,B}) \tag{III.8}$$

The isobaric heats Q^0_{form} (or $-\Delta H^0$) of formation of compounds from the elements may be found in the physico-chemical, thermochemical or thermodynamic handbooks. The following standard condi-

* The numerical factors a_0, a_1, and a_2 can be found in chemical and physico-chemical handbooks, for instance, in [7].

tions are assumed: the temperature of 25 °C, the pressure of $1.01 \times \times 10^5$ Pa and the concentration of 1 mole per 1 kg of the solvent for dissolved compounds. Gases and solutions are assumed to be ideal.

The heat effect of the reaction is the sum of the formation heats of the starting compounds minus the sum of the formation heats of the reaction products:

$$\Delta H = \sum (\Delta H_{\text{form}})_{\text{start}} - \sum (\Delta H_{\text{form}})_{\text{prod}} \qquad \text{(III.9)}$$

To determine the temperature dependence of the heat effect of the reaction the Nernst equation is used:

$$Q_r = Q_r^0 + \Delta a_0 T \pm \frac{1}{2} \Delta a_1 T^2 \pm 1/3 \Delta a_2 T^3 \qquad \text{(III.10)}$$

Here Δa_0, Δa_1, and Δa_2 are the differences of the respective coefficients of Eq. (III.5) for the reaction products and the starting compounds. These coefficients for various reactions are given in chemical handbooks.

The heat Q_e can be found from the loss of heat by the heat-transfer agent, for instance, the heating water. If the amount of heating water is G_w and its specific heat is c_w then

$$Q_e = G_w c_w (t_1 - t_f) \qquad \text{(III.11)}$$

For the steam of the mass G with the evaporation heat r the loss of heat is

$$Q_e = Gr \qquad \text{(III.12)}$$

The loss of heat through the heating wall is

$$Q_e = k_t F (t_a - t_m) \tau \qquad \text{(III.13)}$$

where k_t is the heat transfer coefficient, F is the heat-transfer surface, t_a is the mean temperature of the heating agent (water, steam, etc.), t_m is the mean temperature of the mixture being heated and τ is the time of heating.

Eq. (III.13) and other heat transfer formulas can be used for calculating removal of heat from the reaction mixture in the apparatus or the loss of heat Q_e' into the environment. This consumption of heat is often calculated from the variation of the heat of the cooling agent, for instance, air or water.

The heat per 1 second (in J/s) produced by combustion of fuel or by transformation of the electric energy into the thermal energy is found from the following formulas:

for combustion furnaces

$$Q_e = BQ_l^c \qquad \text{(III.14)}$$

for electric furnaces

$$Q_e = \beta N \qquad \text{(III.15)}$$

Here B is the consumption of fuel (in m^3/s or kg/s), Q_l^c is the lowest heat of combustion of the fuel (in J/m^3 or J/kg), N is the power of the furnace, and β is a dimension factor.

Calculations of the heat of combustion of a fuel from its elemental composition are typically made in technology with the Mendeleev formula:

$$Q_l^c = 339.3C + 1256H - 109(O - S) - 25.2(9H + W) \qquad \text{(III.16)}$$

where C, H, O, and S are, respectively, the concentrations (in % by mass) of carbon, hydrogen, oxygen, and sulphur in the fuel, and W is the moisture content of the fuel (which contains also ash and nitrogen).

The highest heat of combustion Q_h^c is found with the assumption that the moisture produced with combustion and the moisture contained in the fuel are condensed to water from the flue gases and cooled to the initial temperature of the fuel. This heat of combustion is given by the formula

$$Q_h^c = Q_l^c + 25.2\,(9H + W) \qquad \text{(III.17)}$$

The theoretical consumption G_{th} of air (in kilograms per 1 kg of the fuel) can be found from the elemental composition of the fuel with the following equation:

$$G_{th} = 0.116C + 0.348H + 0.0435\,(S - O) \qquad \text{(III.18)}$$

The heat I_{air} supplied by the humid air is given by the equation

$$I_{air} = \alpha G_{th}\,(1.02 + 1.95x)\,t_{air} \qquad \text{(III.19)}$$

where α is the excess ratio for air (in practice α for solid fuel varies from 1.3 to 1.7, for liquid fuel from 1.1 to 1.2 and for gaseous fuel from 1.0 to 1.2), 1.02 is the specific heat of air, 1.95 is the specific heat of steam, x is the moisture content of air (in kilograms per 1 kg of dry air), and t_{air} is the temperature of the air supplied for fuel combustion.

Calculations of the Heats of Chemical and Physical Transformations. Consumption Coefficients

Problem 1. Calculate the heat (in kilojoules) liberated with production of 100 litres of acetylene from calcium carbide. The relevant heats of formation (in kJ/kmole) are: CaC_2—62 700, H_2O—241 840, CaO—635 100, C_2H_2—226 750.

Solution. Acetylene is formed in the reaction

$$CaC_2 + H_2O \rightleftharpoons CaO + C_2H_2 + Q$$

$Q = 635\,100 - 226\,750 - 62\,700 - 241\,840 = 635\,100 - 531\,350 = 103\,750$ kJ/kmole. The amount of heat liberated with formation of 100 litres of acetylene is $103\,750 \times 100/22.4 \times 1000 = 463$ kJ (110.5 kcal).

Problem 2. Find the amount of heat liberated with combustion of 1 m^3 and 1 kg of ethane. The combustion heat for ethane under standard conditions is 1 559 880 kJ/kmole.

Solution. The heat liberated with combustion of 1 m^3 of ethane is $1\,559\,880/22.4 = 69\,700$ kJ (16 650 kcal), the heat for 1 kg is $1\,559\,880/30 = 52\,000$ kJ (12 420 kcal) (30 is the molecular mass of ethane).

Problem 3. Find the theoretical calorific value of coal pyrite (in kJ/kg) containing 45% S and 5% C. The combustion heat of pure dyrites is 7060 kJ/kg and the combustion heat of pure carbon is 32 700 kJ/kg. Combustion may be described by the following reaction equations:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 + Q$$

$$C + O_2 \rightarrow CO_2 + Q$$

Solution. Pure pyrite contains $64 \times 100/120 = 53.35\%$ S (the molecular mass of FeS_2 is 120). Hence, 1 kg of the coal pyrite contains $45/53.35 = 0.842$ kg of pyrite, 0.05 kg of carbon, and 0.108 kg of dirt. Hence, the combustion heat is $7060 \times 0.842 + 32\,700 \times 0.05 = 7575$ kJ/mole.

Problem 4. Derive a formula for finding the calorific value of pyrite according to the content of sulphur in it (n % by mass). The heats of formation: Fe_2O_3—821.3 kJ/mole, SO_2—296.90 kJ/mole, FeS_2—177.4 kJ/mole.

Solution. Combution of pure pyrite is described by the following reaction equation:

$$4FeS_2 + 11O_2 \rightleftharpoons 2Fe_2O_3 + 8SO_2 + Q$$

The heat Q can be found from the formation heats of the compounds:

$$Q = (2 \times 821.3 + 8 \times 296.9) - 4 \times 177.4 = 3208 \text{ kJ}$$

Hence, combustion of 1 kg of pyrite liberates $(3208/4 \times 120) \times 1000 = 6683$ kJ. The heat Q depends on sulphur content of pyrite. If the pure pyrite contains 53.45% of sulphur then for pyrite containing n% of sulphur we have $Q = 6683n/53.35 = 125.3n$ kJ/kg.

Problem 5. Find the combustion temperature for zinc blende containing 96% ZnS if the flue gases contain 7% SO_2, 11% O_2, and 82% N_2 and the furnace losses of heat are 13% of the total heat liberated with combustion (without additional cooling). The degree of combustion of ZnS is 98%.

Solution. Combustion of zinc blende can be described by the equation

$$2ZnS + 3O_2 = 2SO_2 + 2ZnO + 929\,510 \text{ kJ}$$

As the degree of combustion is 0.98 the liberated heat is 929 510 × × 0.98 = 910 920 kJ. Two moles of ZnS (molecular mass 97.4—2 × 97.4) yield 2 moles of SO_2 (2 × 22.4 m^3).

The flue gas contains 82% N_2 and 7% SO_2. The amount of nitrogen remains unchanged in the reaction so that $V_{N_2} = 82 \times 22.4/7 = 263$ m^3 and $V_{O_2} = 11 \times 22.4/7 = 35$ m^3. The total amount of the gas is 263 + 22.4 + 35 = 320.4 m^3. The loss of heat from the furnace to the environment is 464 755 × 0.13 = 60 420 kJ. The remaining amount of heat is 464 755 — 60 420 = 404 335 kJ. The specific heats at 900 °C: $c_{N_2} = 1.382$ kJ/m^3 K, $c_{O_2} = 1.482$ kJ/m^3 K, $c_{SO_2} = 2.215$ kJ/m^3 K. Eq. (III.4) yields

$$t = Q/Gc = 404\,335/(263 \times 1.382 + 35 \times 1.482 + 22.4 \times 2.215) = 869\ ^\circ C$$

Problem 6. Derive a formula for finding the calorific value of the zinc blende containing n% of sulphur.

Solution. Pure ZnS (the molecular mass 97.4) contains 32 × × 100/97.4 = 32.9% of sulphur (the molecular mass 32). The overall combustion reaction for zinc blende can be described by the equation

$$ZnS + 1.5O_2 = ZnO + SO_2 + Q$$

The heats of formation at 25 °C (in kJ/mole): ZnO—349.0, ZnS—201.0, SO_2—296.90. The heat $Q_{25} = 349.0 + 296.90 - 201 = 444.90$ kJ/mole. Hence, combustion of 1 kg of ZnS produces 444.90 × 1000/97.4 = 4568 kJ/kg. If the ore contains n% of sulphur (in ZnS) $Q = 4568n/32.9 \approx 139.0$, n kJ/kg. Under the real combustion conditions at 800-900 °C (since the heat effect of the reaction depends on the temperature) we have $Q = 139.0\ n$ kJ/kg.

Problem 7. Calculate the theoretical temperature of combustion of ethane (the combustion heat 1.56 × 10^6 kJ/kmole) with the 20% excess of air (the excess ratio $\alpha = 1.2$).

Solution. With the given excess of oxygen the combustion reaction for ethane is described by the following equation:

$$C_2H_6 + 3.5O_2 + 0.7O_2 + (4.2 \times 79/21)\,N_2 = 2CO_2 + 3H_2O\ (\text{steam}) + 0.7O_2 + 4.2 \times 3.76N_2$$

If the initial temperature of ethane and air is 0 °C and the combustion temperature is t we can write

$$Q = 1\,560\,997 = (2c_{CO_2} + 3c_{H_2O} + 0.7c_{O_2} + 4.2 \times 3.76c_{N_2})\,t$$

Let us make calculations for t = 1900 °C and t = 2000 °C. The specific heats in kJ/mole K at 1900 and 2000 °C: CO_2—54.20 and 54.50; O_2—35.10 and 35.30; H_2O (steam)—43.2 and 43.6; N_2—33.20 and 33.40.

Hence, at 1900 °C the heat accumulated by the combustion products is

$$Q' = (2 \times 54.20 + 3 \times 43.20 + 0.7 \times 35.10 + 4.2 \times 3.76 \times 33.20) \times 1900 = 1\,495\,042 \text{ kJ}$$

that is $Q' < Q$.

At 2000 °C the heat accumulated by the combustion products is

$$Q'' = (2 \times 54.50 + 3 \times 43.6 + 0.7 \times 35.30 + 4.2 \times 3.76 \times 33.40) \times 2000 = 1\,583\,800 \text{ kJ}$$

that is, $Q'' > Q$.

Let us interpolate the results:

$$Q'' - Q' = 1\,583\,800 - 1\,495\,042 = 88\,758 \text{ kJ}$$

$$\Delta t = 2000 - 1900 = 100 \text{ °C}$$

$$Q - Q' = 1\,560\,997 - 1\,495\,042 = 65\,955 \text{ kJ}$$

$$\Delta t = t - 1900$$

Hence, $\Delta t = 65\,955 \times 100/88\,758 = 74.3$ °C. We obtain $t = 1900 + 74.3 = 1974.3$ °C.

Problem 8. Calculate the theoretical temperature for combustion of the natural-gas methane (the combustion heat 890 310 kJ/mole) with the air excess of 25%.

Solution. Combustion of methane is described by the following reaction equation:

$$CH_4 + 2O_2 + 0.5O_2(\text{excess}) + 2.5 \times 3.76N_2 = CO_2 + 2H_2O(\text{steam}) + 0.5O_2 + 2.5 \times 3.76N_2$$

If the initial temperature of methane and air is 0 °C the heat balance at the combustion temperature t is given by the equation:

$$Q = 890\,310 = (c_{CO_2} + 2c_{H_2O} + 0.5c_{O_2} + 2.5 \times 3.76c_{N_2})\,t$$

The specific heats of the combustion products in kJ/kmole K at 1800 and 1900 °C: O_2—34.9 and 35.1; CO_2—53.9 and 54.2; N_2—33.1 and 33.2; H_2O (steam)—42.8 and 43.2.

The heat of the products at 1800 °C is

$$Q' = (53.9 + 2 \times 42.8 + 0.5 \times 34.9 + 2.5 \times 3.76 \times 33.1) \times 1800 = 842\,000 \text{ kJ} < Q = 890\,310 \text{ kJ}$$

The heat of the products at 1900 °C is

$$Q'' = (54.2 + 2 \times 43.2 + 0.5 \times 35.1 + 2.5 \times 3.76 \times 33.2) \times 1900 = 906\,000 \text{ kJ} > Q = 890\,310 \text{ kJ}$$

Let us interpolate the results: $\Delta t = 1900 - 1800 = 100$ °C

$$Q'' - Q = 906\,000 - 890\,310 = 15\,690 \text{ kJ}$$

$$Q - Q' = 890\,310 - 842\,000 = 48\,310 \text{ kJ}$$

$$\Delta t = t - 1800$$

$$\Delta t = 15\,690 \times 100/58\,310 = 26.8 \text{ °C}$$

$$t = 1800 + 26.8 = 1826.8\text{°C}$$

Problem 9. Calculate the variation of temperature in the reaction of oxidation of SO_2 to SO_3 if the degree of oxidation is 0.55 and 0.96. The mean specific heat of the mixture of the gases (containing 8% SO_2, 11% O_2 and 81% N_2) is assumed to be constant (1.382 kJ/m³ K). The combustion heat is 94 400 kJ/kmole.

Solution. The oxidation reaction may be described by the equation

$$SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3 + 94\,400 \text{ kJ/kmole}$$

Then for 100 m³ of the gas mixture we obtain $Q_1 = 8 \times 0.55 \times \times 94\,400/22.4 = 18\,480$ kJ; $Q_2 = 8 \times 0.96 \times 94\,400/22.4 = = 32\,200$ kJ. The volume of the product mixture is $V_1 = 100 - - 8 \times 0.55 \times 0.5 = 97.8$ m³ and $V_2 = 100 - 8 \times 0.96 \times 0.5 = = 96.16$ m³. Hence, $\Delta t_1 = 18\,480/1.382 \times 97.8 = 138$ °C, $\Delta t_2 = = 32\,200/1.382 \times 96.16 = 244$ °C.

Problem 10. Calculate the temperature increase with 1% oxidation of SO_2 at 500 °C for the gas mixture containing 7% SO_2, 12% O_2 and 81% N_2. The oxidation reaction is described by the equation

$$SO_2 + \frac{1}{2} O_2 \rightleftarrows SO_3 + 94\,400 \text{ kJ}$$

The specific heats (in kJ/m³ K): $c_{SO_2} = 2.082$, $c_{O_2} = 1.402$, $c_{N_2} = = 1.343$. The heat effect of the reaction depends on the temperature according to the following formula: $Q = 4.187\,(24\,555 - - 2.21T)$ kJ/kmole.

Solution. The heat of the reaction at 500 °C is $Q_{500} = 4.187 \times \times (24\,555 - 2.21 \times 773) = 100\,790$ kJ/kmole. The amount of SO_2 reacting per 1 m³ of the gas mixture is $0.07/22.4 = 0.312 \times 10^{-4}$ kmole. The respective amount of heat liberated in the reaction is $100\,790 \times 0.312 \times 10^{-4} = 3.144$ kJ. The specific heat of the gas mixture is $0.07 \times 2.082 + 0.12 \times 1.402 + 0.81 \times 1.343 = = 1.402$ kJ/m³ K.

The temperature of 1 m³ of the gas mixture increases owing to the reaction by $\Delta t = Q/cV = 3.144/1.402 \times 1 = 2.24$ K.

Problem 11. Determine the theoretical temperature in the lime kiln if the air excess is 2 and 3 and pure carbon is used. The heat effects of the reactions occurring in the kiln and the heat losses may be ignored.

Solution. The amount of air needed for complete combustion of 1 kg of carbon in the reaction

$$C + O_2 \rightarrow CO_2$$

is $32 \times 100/12 \times 23.3 = 11.95$ kg (here 23.3 (% by mass) is the oxygen content of the air).

With the air excess ratio of 2 and 3 the needed amount of air is 23.9 and 35.85 kg, respectively.

The calorific value of carbon is 32 784 kJ/kg. The specific heat of air in the 0-900 °C range is 1.038 kJ/kg K.

For the air excess ratio of 2 the theoretical temperature in the lime kiln is $32\,784/23.9 \times 1.038 = 1321$ °C. This calculation does not take into account the composition of the charge, the degree of combustion of the coke, heat losses, etc.

For the air excess ratio of 3 the theoretical temperature is $32\,784/35.85 \times 1.038 = 881$ °C. This temperature is not sufficient for the dissociation of lime which occurs at temperatures above 1000 °C in the kiln. Hence, the air excess ratio for the lime kiln should be not more than 2-2.3.

Problem 12. The lime kiln is charged with 10 tons of lime and with coke containing 91% C, 7% ashes, and 2% moisture. Find (1) coke consumption, (2) the composition of the flue gas (in % by volume), and (3) the heat effect of the reaction. The formation heats for the compounds (in kJ/kmole): $CaCO_3$—1 206 000, CaO—635 100, CO_2—393 510. The degree of dissociation of lime is 95.0%. The air excess ratio is 1.4.

Solution. (1) The reaction of lime dissociation is described by the equation

$$CaCO_3 \rightleftarrows CaO + CO_2 - Q$$

The heat effect of dissociation of 1 kmole (100 kg) of $CaCO_3$ is $Q = 635\,100 + 393\,510 - 1\,206\,000 = -177\,390$ kJ. As the degree of dissociation is 0.95 the required amount of heat is $177\,390 \times 0.95 = 168\,520$ kJ.

The calorific value for pure carbon is 32 784 kJ/kg. Hence, the amount of pure carbon required for roasting 10 tons of lime is $168\,520 \times 10\,000/32\,784 \times 100 = 514$ kg providing that carbon is completely oxidized to CO_2. As the coke contains 91% C the required amount of coke is $514 \times 100/91 = 564$ kg.

(2) Let us find the composition of the flue gas.

CO_2: (a) the amount produced with dissociation of 10 tons of lime is $95 \times 22.4 \times 10 \times 1000/100 \times 100 = 2128$ m³; (b) the amount produced with coke burning in the reaction $C + O_2 \rightarrow CO_2$ is $514 \times 22.4 \times 1000/12 = 959\,500$ m³. The total amount of CO_2 is $2128 + 959\,500 = 961\,628$ m³.

O_2: The volume of oxygen consumed in coke burning is equal to the volume of carbon dioxide produced with it, that is, 959 500 m³.

Since the air excess ratio is 1.4 the amount of oxygen fed to the kiln is 959 500 × 1.4 = 1 343 300 m³. The amount of oxygen remaining in the flue gas is 1 343 300 — 959 500 = 383 800 m³.

N_2: The amount of nitrogen in the air fed to the kiln is 1 343 300 × × 79/21 = 5 060 000 m³.

Hence, the flue gas has the following composition: carbon dioxide—961 628 m³ (15.03%); oxygen—383 800 m³ (6.0%); and nitrogen—5 050 800 (78.97%). The total volume of the flue gas is 6 396 228 m³.

Problem 13. Find the heat liberated with roasting of 1 ton of pyrite containing 38% of sulphur if the degree of combustion of sulphur is 0.96. Combustion of pyrite is described by the following equation:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 + Q$$

Q = 3413.2 kJ. Pure FeS_2 contains 53.35% of sulphur and 46.65% of iron.

Solution. 1 ton of pure FeS_2 contains 533.5 kg of sulphur. The amount of sulphur entering the combustion reaction (per 1 ton of pyrite) is 380 × 0.96 kg. Hence the respective amount of pure FeS_2 is 1000 × 380 × 0.96/533.5 = 682 kg.

According to the reaction equation combustion of 480 kg of FeS_2 yields 3413.2 × 10³ kJ. Then, combustion of 682 kg of FeS_2 yields 3413.2 × 10³ × 682/480 = 4 849 600 kJ.

Problem 14. 10 000 m³/h of the gas mixture containing 10% SO_2, 11% O_2, and 79% N_2 are fed to the first bed of the contact apparatus at 450 °C. The exothermic reaction is described by the reaction $SO_2 \times \frac{1}{2} O_2 \rightleftarrows SO_3 \times Q'$ (where $Q' = 101\,420 - 9.26\,T_m$ (kJ/kmole)). The mean temperature T_m is found from the initial temperature T_1 and the final temperature T_f: $T_m = (T_f - T_1)/2.3 \log T_f/T_1$. The final temperature of the gas mixture is 580 °C. The specific heat of the gas mixture is assumed to be constant: c = = 1.38 kJ/m³ K. The volume variation with reaction is ignored. Find the degree of oxidation of SO_2 to SO_3.

Solution. $T_f - T_1 = 580 - 450 = 130$ K. $Q = cV(T_f - T_1) =$ = 1.38 × 10 000 × 130 = 1 794 000 kJ. $T_m = (853 - 723)/2.3 \log 853/723 = 130/2.3 \times 0.072 = 785$ K. $Q' = 101\,420 - 9.26 \times$ × 785 = 94 150 kJ/kmole. $V_{SO_3} = 1\,794\,000 \times 22.4/94\,150 =$ = 426 m³. Hence, the degree of oxidation of SO_2 is 426/1000=0.426.

Problem 15. Determine the theoretical consumption of fuel oil for production of 1 ton of aluminium oxide from aluminium hydroxide. The calorific value for fuel oil is 41 870 kJ/kg. The formation heats: Al $(OH)_3$—1 243 kJ/mole, Al_2O_3—1 676 kJ/mole, H_2O—241.84 kJ/mole.

Solution. Aluminium oxide is produced in the following reaction:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

The heat effect of the reaction is $1676 + 3 \times 241.84 - 2 \times 1243 = -84.5$ kJ/mole. Hence, the amount of heat needed to produce 1 ton of aluminium oxide is $84.5 \times 10^3 \times 1000/102 = 828\,000$ kJ (here 102 is the molecular mass of Al_2O_3). Thus, the amount of fuel oil needed to supply the heat is $828\,000/41\,870 = 18.9$ kg.

Problem 16. Calculate the consumption of natural gas (containing 82% CH_4 and 9% of higher hydrocarbons) with the calorific value of 33 950 kJ/m³ needed for production of 100 tons a day of alumina Al_2O_3 in the roasting furnace. The heat losses to the environment amount to 5% of the total heat consumption. The temperature at the reaction zone is 1200 °C. The temperature of the materials fed to the furnace is 20 °C. The compounds have the following formation heats (in kJ/mole): Al $(OH)_3$—1243, Al_2O_3—1676, and H_2O—241.84. The specific heat of the reaction mixture is 0.879 kJ/kg at 20 °C for Al_2O_3 and H_2O and 1.327 kJ/kg and 38.14 kJ/kmole at 1200 °C.

Solution. The process is described by the following reaction:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O - Q$$

Molecular masses: 2Al $(OH)_3$—156, Al_2O_3—102, $3H_2O$—54

The consumption of Al $(OH)_3$ and the amount of water produced in the reaction per day are: $G_{Al(OH)_3} = 10^5 \times 156/102 = 15.3 \times 10^4$ kg and $G_{H_2O} = 10^5 \times 54/102 = 5.3 \times 10^4$ kg. The input of heat with Al hydroxide is

$$Q_{Al(OH)_3} = 15.3 \times 10^4 \times 0.879 \times 20 = 2\,689\,740 \text{ kJ}$$

The consumption of heat for the reaction is:

$$Q_r = (15.3 \times 10^4/156) \times 10^3 \times (1676.0 + 3 \times 241.84 - 2 \times 1243) = -94\,644\,000 \text{ kJ}$$

The amount of heat removed with Al_2O_3 is

$$Q_{Al_2O_3} = 100 \times 10^3 \times 1.327 \times 1200 = 159\,240\,000 \text{ kJ}$$

The amount of heat carried by H_2O is

$$Q_{H_2O} = 5.3 \times 10^4 \times 38.14 \times 1200/18 = 134\,760\,000 \text{ kJ}$$

The total consumption of heat is 388 644 000 kJ. The losses of heat to the environment are $0.05 \times 388\,644\,000 = 19\,432\,200$ kJ. Hence, the amount of heat which should be supplied through burning natural gas is $388\,644\,000 + 19\,432\,200 - 2\,689\,740 = 405\,386\,460$ kJ. The volume of gas which should be burned is $405\,386\,460/33\,950 = 11\,940$ m³.

Problem 17. The sulphate process for production of hydrochloric acid is described by the following equation:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl - Q$$

Calculate the heat effect of the reaction and the consumption of fuel per 1 ton of hydrogen chloride (neglecting the heat of the materials).

The formation heats (in kJ/kmole): NaCl—410 900, Na_2SO_4—1 384 000, H_2SO_4—811 300, HCl—92 300. The coke-oven gas used as fuel has the following composition: H_2—56%, CH_4—25%, C_2H_4—2.5%, CO—7%, CO_2—2.6%, O_2—0.7%, N_2—5.7%. The calorific values (in kJ/kmole): H_2—285 840, CH_4—890 310, C_2H_4—1 410 970, CO—283 010.

Solution. The heat effect of the reaction is $Q = 1\,384\,000 + 2 \times 92\,300 - (2 \times 410\,900 + 811\,300) = -64\,500$ kJ.

The amount of heat consumed in production of 1 ton of HCl is $Q' = 1000 \times 64\,500/73 = 883\,560$ kJ (73 is the molecular mass of 2HCl).

The calorific value of the coke-oven gas is $285\,840 \times 0.56 + 890\,310 \times 0.25 + 1\,410\,970 \times 0.025 + 283\,010 \times 0.07 = 437\,732$ kJ/kmole.

Hence, the amount of the coke-oven gas consumed in production of 1 ton of HCl is 883 560/437 732 = 2.04 kmole or $2.04 \times 22.4 = 45.7$ m³.

Problem 18. The final reaction mixture in chlorination of benzene contains 39% of chlorobenzene, 1% of dichlorobenzene, and 60% of benzene. Find the amount of heat liberated in the reaction per 1 ton of benzene. The heats of formation (in kJ/mole) of benzene—49.063, chlorobenzene—52.17, dichlorobenzene—53.05, hydrogen chloride—92.36.

Solution. Considerable amounts of heat (about 117 kJ/mole) are liberated with chlorination of benzene. In the continuous process the reaction mixture is heated to the boiling point (76-85 °C) and a significant part of the liberated heat is consumed for vaporization of benzene The process is described by the following equations:

$$C_6H_6 + Cl_2 \rightleftharpoons C_6H_5Cl + HCl \quad (1)$$

$$C_6H_6 + 2Cl_2 \rightleftharpoons C_6H_4Cl_2 + 2HCl \quad (2)$$

The molecular masses: C_6H_6—78, C_6H_5Cl—112.5, $C_6H_4Cl_2$—146.

The consumption of benzene to produce 39 kg of chlorobenzene contained in 100 kg of the reaction mixture is $39 \times 78/112.5 = 27.3$ kg. The consumption of benzene to produce 1 kg of dichlorobenzene contained in 100 kg of the reaction mixture is $1 \times 78/147 = 0.53$ kg. As 100 kg of the mixture contain 60 kg of unreacted benzene the total consumption of benzene to produce 100 kg of the mixture is 87.83 kg.

Hence, 1 ton of benzene gives rise to 1000 × 100/87.83 = 1140 kg of the reaction mixture containing 1140 × 0.39 = 445 kg of chlorobenzene, 1140 × 0.01 = 11.4 kg of dichlorobenzene and 1140 × × 0.6 = 683.6 kg of benzene.

The heat effect of reaction (1) is 52.17 + 92.36 — (—49.063) = = 193.593 kJ/mole and the heat effect of reaction (2) is 53.05 + + 2 × 92.36 — (—49.063) = 286.833 kJ/mole.

The heat liberated with chlorination of 1 ton of benzene is 193.593 × 445 × 1000/112.5 × 286.833 × 11.4 × 1000/147 = = 797 318 kJ.

Problem 19. The carbonization gas from brown coal has the following composition (in % by volume): CH_4—60, H_2—20, other hydrocarbons (calculated as C_2H_4)—3, CO—6, CO_2—6.8, O_2—0.04, N_2—4.16.

Find the amount of dry air needed for complete combustion of the gas for the air excess ratio of 1.2, the composition of the combustion products, and the calorific value of the gas (in kJ/m³). The calorific values of the gas components are (in kJ/kmole): CH_4—890 310, C_2H_4—1 410 970, H_2—285 840, CO—283 010.

Solution. Carbonization of solid fuel is carried out at 500-600 °C in the absence of air. The process yields gas which has a high calorific value and can be used as a high-quality fuel or as a raw material in chemical industry. The calculations will be made for 1000 m³ or 1000 kmole of the gas. Full combustion of the gas is described by the following reaction equations:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1)$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (2)$$

$$H_2 + 0.5O_2 \rightarrow H_2O \quad (3)$$

$$CO + 0.5O_2 \rightarrow CO_2 \quad (4)$$

Equations (1)-(4) show that the following amounts of oxygen are needed for combustion of the gas components: methane—600 × × 2 = 1200 m³, ethylene—30 × 3 = 90 m³, hydrogen—200 × × 0.5 = 100 m³, carbon monoxide—60 × 0.5 = 30 m³. The total consumption of oxygen per 1000 m³ of the gas is 1420 m³.

Hence, the amount of oxygen which should be supplied for combustion of 1000 m³ of the gas is 1420 m³ — 0.4 m³ = 1419.6 m³ (since the gas contains 0.04% O_2).

The nitrogen-oxygen ratio for the air is 79/21 = 3.76. Hence, the theoretical consumption of air is 1419.6 + 3.76 × 1419.6 = = 6760 m³. As the air excess ratio is 1.2 the actual consumption of air is 6760 × 1.2 = 8120 m³ or 8120 × 1.293 = 10 150 kg.

Composition of the combustion products: (in m^3):

	CO_2	H_2O (steam)
Reaction (1)	600	1200
Reaction (2)	60	60
Reaction (3)	—	200
Reaction (4)	60	—
Total:	720	1460

The total content of carbon dioxide in the combustion products is $720 + 68 = 788$ m^3 or $788 \times 44/22.4 = 1546$ kg. The mass of 1460 m^3 of steam is $1460 \times 18/22.4 = 1174$ kg. The nitrogen content in the combustion products (including the nitrogen of the gas) is $5\,340.4 \times 1.2 + 38 = 6448$ m^3 or $6448 \times 28/22.4 = 8050$ kg.

The oxygen content in the combustion products is $1419.6 \times \times 1.2 - 1419.6 = 282$ m^3 or $282 \times 32/22.4 = 403$ kg.

The combustion products have the following composition (per 1000 m^3 of the gas):

Product	kg	% by mass	m^3	% by volume
CO_2	1 546	13.7	788	7.9
O_2	403	3.5	282	3.2
N_2	8 050	72.3	6448	72.6
H_2O	1 174	10.5	1460	16.3
Total:	11 173	100	8978	100

To calculate the calorific value of the gas we should find the molar fractions for each of the gas components: CH_4—$0.6/22.4 = 0.0268$, C_2H_4—$0.03/22.4 = 0.0013$, H_2—$0.2/22.4 = 0.009$, CO—$0.06/22.4 = = 0.0026$. Hence, the heat liberated with combustion of 1 m^3 of the gas can be found as the sum of the heats of combustion of the gas components: CH_4—$0.0268 \times 890\,310 = 23\,880$ kJ, H_2—$0.009 \times \times 285\,840 = 256$ kJ, C_2H_4—$0.0013 \times 1\,410\,970 = 1836$ kJ, CO—$0.0026 \times 283\,010 = 736$ kJ. Thus, the heat liberated with combustion of 1 m^3 of the carbonization gas is 26 708 kJ or 6390 kcal.

Problem 20. Find the heat effect for gasification of solid fuel producing gas of the following composition (in % by volume): CO—38, H_2—50, CO_2—6.2, and N_2—5.8. The formation heats (in kJ/mole): CO—110.58, CO_2—393.79, H_2O (steam)—242.

Solution. The process of gasification can be described by the following equations (see Chapter I, Problem 6):

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

Calculations will be made for 1000 m^3 of the producer gas. As the gas contains 38% CO reaction (1) yields $380 + 62 = 442$ m^3 of CO (62 m^3 of CO are consumed in reaction (2)). Reaction (2) gives rise to 62 m^3 of CO_2.

Hence, the heat effect of reactions (1) and (2) is

$$Q = q_{CO} - q_{H_2O} + q_{CO_2} - q'_{CO} - q'_{H_2O} = 110.58 \times 1000 \times \times 442/22.4 - 242 \times 1000 \times 442/22.4 + 393.79 \times 1000 \times \times 62/22.4 - 110.58 \times 1000 \times 62/22.4 - 242 \times 1000 \times \times 62/22.4 = -2\,511\,477 \text{ kJ}$$

Another approach can be used to solve this problem. Since 1000 m³ of the gas contain 380 m³ of CO, 500 m³ of H_2, and 62 m³ of CO_2 and 500 m³ of H_2O were used for gasification we obtain $Q = q_{CO} + + q_{CO_2} - q_{H_2O} = 380 \times 1000 \times 110.58/22.4 + 62 \times 1000 \times \times 393.79/22.4 - 500 \times 1000 \times 242/22.4 = -2\,476\,000$ kJ.

Problem 21. A saturator contains 130 kg of the 76% solution of sulphuric acid, and 34 kg of the gaseous ammonia bubbles through the solution. The heat losses to the environment amount to 9% of the total heat. Find the amount of heat which can be used for evaporation of water. The initial temperature of the acid and ammonia is 25 °C.

	Molecular mass	Formation heat, kJ/kmole	Specific heat at 25 °C, kJ/kmole K
H_2SO_4	98	811 300	137 570
NH_3	17	46 190	35 650
$(NH_4)_2SO_4$	132	1 179 300	187 070

Solution. To remove ammonia from industrial and waste gases they are bubbled through sulphuric acid solution. For instance, this method is used to remove NH_3 from the coke-oven gas. The reaction is described by the following equation:

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + Q$$

The heat effect of the reaction is $Q = 1\,179\,300 - (811\,300 + + 2 \times 46\,190) = 275\,620$ kJ/kmole.

The amount of H_2SO_4 in the reaction mixture is $0.76 \times 130 = = 99$ kg. The amount of heat supplied with the reactants is $99 \times \times 137\,570/98 + 34 \times 35\,650/2 \times 17 = 174\,596$ kJ/kmole. The total amount of heat is $174\,596 + 275\,620 \times 99/98 = 452\,972$ kJ. This heat minus the heat losses ($452\,972 \times 0.09 = 40\,767$ kJ) is available for evaporation of water: $452\,972 - 40\,767 = 412\,205$ kJ.

Problem 22. Find the combustion temperature for the fuel oil with the following composition (in % by mass): C—87, O_2—1.0, H_2—10.8, S—0.7, and N_2—0.5. The air contains 0.015 m³ of moisture per 1 m³. The air excess ratio is 1.36. The initial temperature of the fuel oil and air is 20 °C. The heat losses (from the furnace walls and the flame) amount to 6.5% of the total heat.

Solution. Complete combustion is described by the following equations:

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad (2)$$

$$S + O_2 \rightarrow SO_2 \quad (3)$$

Calculations will be made for 1 kg of the fuel oil. According to the Mendeleev's formula (III.16) the lowest combustion heat for the fuel oil is $393.3 \times 87 + 1256 \times 10.8 - 109\,(1 - 0.7) - 25.2 \times (9 \times 10.8) = 45\,297.3$ kJ = 10 800 kcal. If the mean specific heat of the fuel oil is 2.5 kJ/kg K the amount of heat brought by 1 kg of the oil at 20 °C is $ct = 50$ kJ.

To find the consumption of air let us calculate the consumption of oxygen: reaction (1)—$32 \times 870/12 = 2320$ g, reaction (2)—$16 \times 108/2 = 864$ g, reaction (3)—$7 \times 32/32 = 7$ g. The total consumption of oxygen is 3191 g and as the oil contains 10 g of oxygen the amount of oxygen supplied for combustion is $3.191 - 0.01 = 3.181$ kg or $22.4 \times 3.181/32 = 2.22$ m³. As the air excess ratio is 1.36 the actual consumption of oxygen is $2.22 \times 1.36 = 3.02$ m³. The consumption of nitrogen is $3.02 \times 3.76 = 11.38$ m³ and the total amount of air is 14.4 m³ or $14.4 \times 1.2928 = 18.62$ kg. The moisture content of 1 kg of air is $0.015 \times 18/1.2928 \times 22.4 = 0.0093$ kg.

The specific heat of the dry air is 28.35 kJ/kmole K and that of the air moisture is 33.71 kJ/kmole K. Then the amount of heat brought to the furnace by the air at 20 °C is $14.4 \times 28.35 \times 20/22.4 +$

TABLE 19

Components of fuel and air		Combustion products, kmole				
Component	kmole	CO_2	H_2O	SO_2	N_2	O_2
C	$0.87/12 = 0.075$	0.075				
H_2	$0.108/2 = 0.054$		0.054			
S	$0.007/32 = 0.0002$			0.0002		
N_2 (fuel)	$0.005/28 = 0.00018$				0.00018	
N_2 (air)	$11.38/22.4 = 0.508$				0.508	
O_2 (excess) 3.02-2.22 = = 0.8 m³	$0.8/22.4 = 0.0357$					0.0357
H_2O (air)	$18.62 \times 0.0013/18 = 0.0014$		0.0014			
Total:		0.075	0.0554	0.0002	0.50818	0.0357

$+ 0.0093 \times 33.71 \times 20 = 364.5$ kJ $+ 60.7$ kJ. Hence, the total amount of heat per 1 kg of oil is $45\,297.3 + 50 + 364.5 + 60.7 = 45\,772.5$ kJ. Hence, the heat losses are $45\,772.5 \times 0.065 = 2975.3$ kJ. The heat removed with the flue gas is $45\,772.5 - 2975.3 = 42\,797.2$ kJ $= Q$.

Table 19 presents the composition of the combustion products (per 1 kg of fuel oil).

The total amount of the combustion products is 0.6745 kmole. The products have the following composition: CO_2—10.98%, H_2O—9.3%, SO_2—0.03%, N_2 — 74.4%, O_2 — 5.24%.

These gases have the following enthalpies (in kJ/kmole):

	1700 °C	1800 °C
CO_2	90 800	96 500
H_2O	71 700	76 700
SO_2	91 100	96 500
N_2	55 700	59 600
O_2	58 400	59 600

The amount of heat of the flue gas at 1700 °C is

$$Q' = 0.075 \times 90\,800 + 0.0554 \times 71700 + 0.0002 \times 91\,100 + \\ + 0.5082 \times 55\,700 + 0.0357 \times 58\,400 = 41\,758 \text{ kJ}$$

It can be seen that $Q' < Q$. The amount of heat at 1800 °C is

$$Q'' = 0.075 \times 96\,500 + 0.0554 \times 76\,700 + 0.0002 \times 96\,500 + \\ + 0.5082 \times 59\,600 + 0.0357 \times 59\,600 = 44\,669 \text{ kJ}$$

We have $Q'' > Q$.

Let us interpolate the results. $Q'' - Q' = 44\,669 - 41\,758 = 2911$ kJ. The temperature difference is $1800 - 1700 = 100$ °C. $Q - Q' = 42\,797.2 - 41\,758 = 1029$ kJ. $\Delta t = t - 1700 = 1029 \times 100/2911 = 35$ °C. Hence, the combustion temperature for the fuel oil is $t = 1700 + 35 = 1735$ °C.

Problem 23. Calculate the combustion temperature for the shale with the following composition: (in % by mass): C—70, H_2—6.5, O_2—10, S—2, N_2—1, ash—5.5, H_2O—5.

The air excess ratio is 1.55. The relative humidity of the air is 100%. The moisture content of the air at 25 °C is 23.1 g/m³. The initial temperature of the shale and air is 25 °C. The heat losses (through the furnace walls and with slag) are 8% of the total heat.

Solution. The combustion reactions are described by the following reactions:

$$C + O_2 \rightarrow CO_2 \quad (1)$$

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad (2)$$

$$S + O_2 \rightarrow SO_2 \quad (3)$$

Calculations will be made for 1 kg of shale.

According to the Mendeleev's formula (III.16) the lowest combustion heat of shale is

$$Q_l^r = 339.3 \times 70 + 1256 \times 6.5 - 109\,(10-2) -$$

$$-25.2\,(9 \times 6.5 - 5) = 29\,650 \text{ kJ/kg} = 7110 \text{ kcal/kg}$$

If the mean specific heat of shale is 0.78 kJ/kg K the amount of heat of 1 kg of shale at 25 °C is $0.78 \times 25 = 18.2$ kJ.

According to Eq. (III.18) the theoretical consumption of air is $0.116 \times 70 + 0.348 \times 6.5 + 0.0435 \times (2 - 10) = 10.05$ kg or $10.05/1.2928 = 7.77$ m³. This amount of air contains $7.77 \times 79/100 = 6.14$ m³ of nitrogen and $7.77 - 6.14 = 1.63$ m³ of oxygen.

The heat of the air supplied to the furnace can be found from Eq. (III.19). The amount of moisture in 1 kg of air is $23.1 \times 7.77/10.05 = 17.9$ g $= 0.0179$ kg. Hence, the heat of the air is $1.55 \times 10.05\ (1.02 + 1.95 \times 0.0179)\ 25 = 392.8$ kJ. The total amount of heat is $29\,650 + 18.2 + 392.8 = 30.061$ kJ.

The heat losses are $30\,061 \times 0.08 = 2410$ kJ. The heat of the flue gas is $Q = 30\,061 - 2410 = 27\,651$ kJ.

Table 20 presents the composition of the combustion products (per 1 kg of shale).

TABLE 20

Components of shale and air		Combustion products, kmole				
component	kmole	CO_2	H_2O	SO_2	N_2	O_2
C	$0.7/12 = 0.058$	0.058				
H_2	$0.065/2 = 0.033$		0.033			
S	$0.02/32 = 0.00062$			0.00062		
N_2 (shale)	$0.01/28 = 0.0004$				0.0004	
N_2 (air)	$6.14 \times 1.55/22.4 = 0.425$				0.425	
O_2 (excess) $1.63 \times 0.55 = 0.9$ m³	$0.9/22 = 0.04$					0.04
H_2O (air)	$1.55 \times 10.05 \times 0.0179/18 = 0.0155$		0.0155			
Total:		0.058	0.0485	0.00062	0.4254	0.04

Enthalpy values for the gases:

	1300 °C	1400 °C		1300 °C	1400 °C
H_2	39 300	42 600	CO_2	66 800	72 700
O_2	43 400	47 606	H_2O	52 200	56 800
N_2	41 600	45 600	SO_2	67 900	73 800

If the temperature of combustion is 1300 °C the heat of the flue gas $Q' = 0.058 \times 66\,800 + 0.0485 \times 52\,200 + 0.00062 \times 67\,900 + 0.4254 \times 41600 + 0.04 \times 43\,400 = 25\,940$ kJ. We can see that $Q' < Q$. If the temperature of combustion is 1400°C we have

$$Q'' = 0.058 \times 72\,700 + 0.0485 \times 56\,800 + 0.00062 \times$$

$$\times 73\,800 + 0.4254 \times 45\,600 + 0.04 \times 47\,606 = 28\,432 \text{ kJ}$$

We have $Q'' > Q$. Let us interpolate the results. We have $Q'' - Q' = 28\,432 - 25\,940 = 2492$ kJ and the temperature difference is $1400 - 1300 = 100$ °C. $Q - Q' = 27\,651 - 25\,940 = 1711$ kJ and $\Delta t = t - 1300$ °C. Hence, $\Delta t = 1711 \times 100/2492 = 69$ °C. The combustion temperature for shale is $t = 1300 + 69 = 1369$ °C.

Calculations of the Heat Balance for Industrial Processes

Problem 24. The density of styrene is $d_4^{20} = 0.906$. The specific heat of styrene is 1.742 kJ/kg K at 20 °C and 2.479 kJ/kg K at 145 °C. The specific heat of polystyrene is 1.457 kJ/kg K at 20 °C and 3.119 kJ/kg K at 145 °C.

Calculate the volume of the polymerizer and draw up the heat balance for the first polymerizer for 1 ton of styrene.

The coefficient of charge is $\varphi = 0.65$ and the operational capacity of 1-ton polymerizer is 1.8 m³.

Solution. The isothermal process for production of block polystyrene is carried out in a battery of polymerizers with disk agitators. Given below are some characteristics of the process:

	t_1, °C	t_f, °C	Degree of polymerization, %	Time of processing, h
Polymerizer I	50	145	48	2
Polymerizer II	145	160	75	2
Polymerizer III	160	180	90	2

Polymerization of styrene giving rise to polystyrene can be described by the following reaction:

$$n\text{C}_6\text{H}_5\text{—CH=CH}_2 \rightarrow (\text{—CH—CH}_2\text{—})_n + 68\,700 \text{ kJ/kmole}$$

$$\text{C}_6\text{H}_5$$

The heat of the reaction was found from the experimental data for the monomer with a molecular mass of 104.

The volume of the polymerizer can be found from the coefficient of charge and the operational capacity: $v = 1.8/0.65 = 2.77$ m³. The heat effect of the polymerization reaction is 68 700/104 = = 661 kJ/kg.

For 1 ton of styrene the heat brought with styrene is 1000 × × 1.742 × 50 = 87 089 kJ and the heat of polymerization is 0.48 × 1000 × 661 = 317 280 kJ. The total input of heat is 404 369 kJ. The heat removed with polystyrene is 3.119 × 145 × × 480 = 217 082 kJ. The heat removed with remaining styrene is 2.479 × 145 × 520 = 186 916 kJ. The total amount of removed heat is 403 998 kJ. There is a small difference between input and output of heat: 404 369 — 403 998 = 371 kJ.

Problem 25. Calculate the heat balance of the apparatus for partial oxidation of SO_2 with a capacity of 25 000 m³/h. The starting gas mixture has the following composition (in % by volume): SO_2—9, O_2—11, N_2—80. The degree of oxidation is 88%. The temperature of the starting gas mixture is 460 °C; the final temperature of the reaction mixture is 580 °C. The mean specific heat of the gas mixture (which is assumed to be constant) is 2.052 kJ/m³ K. The losses of heat are 5% of the total heat.

Solution. The oxidation reaction is described by the following equation:

$$SO_2 + 1/2O_2 \rightleftarrows SO_3 + 94\,207 \text{ kJ/kmole}$$

Table 21 describes compositions of the starting and final gas mixtures (per hour).

TABLE 21

Starting mixture		Final mixture	
Gas	m³	Gas	m³
SO_2	2 250	SO_3	2250×0.88=1980
N_2	20 000	N_2	20 000
O_2	2 750	O_2	2750—1980/2=1760
		SO_2	2250—1980=270
Total:	25 000		24 010

The heat carried by the initial gas is

$$Q_1 = 25\,000 \times 2.052 \times 460 = 23\,598\,000 \text{ kJ}$$

The heat produced by oxidation is

$$Q_2 = 94\,207 \times 2250 \times 0.88/22.4 = 8\,290\,216 \text{ kJ}$$

The total input of heat is

$$\sum Q_{\text{input}} = 31\,888\ \ 216 \text{ kJ}$$

The heat removed with the final gas mixture is

$$Q_3 = 24\,010 \times 2.052 \times 580 = 28\,564\,000 \text{ kJ}$$

The loss of heat is $Q_{\text{loss}} = 31\,888\,216 \times 0.05 = 1\,594\,400$ kJ. The total heat removed is $\sum Q_r = 30\,158\,400$ kJ. Hence the excess heat that should be removed is

$$\sum Q_{\text{input}} - \sum Q_r = 31\,888\,216 - 30\,158\,400 = 1\,729\,816 \text{ kJ}$$

The heat balance is summarized in Table 22.

TABLE 22

The Heat Balance of the Process

Inputs	kJ	%	Outputs	kJ	%
Q_1	23 598 000	73.9	Q_3	28 564 000	89.6
Q_2	8 290 216	26.1	Q_{loss}	1 594 400	5.0
			Q_r	1 729 816	5.4
Total:	31 888 216	100	*Total:*	31 888 216	100

Problem 26. Calculate the heat balance (for 1 hour of operation) for the pyrolysis stage in production of acetic anhydride from acetone. The reactions are described by the following equations:

$$(CH_3)_2CO \xrightarrow{\text{pyrolysis}} CH_2{=}CO + CH_4 - 83.7 \text{ kJ/mole}$$

$$CH_2{=}CO + CH_3COOH \rightleftharpoons (CH_3CO)_2O$$

The temperature of pyrolysis is 800 °C, 24 tons of acetic anhydride per day are produced. The yield of ketene is 0.25. The heat of evaporation of acetone is 553.5 kJ/kg. The specific heats: acetone—2.09 kJ/kg at 20° C, the reaction mixture—2.26 kJ/kg at 800 °C.

Find the amount of natural gas (containing 98% of methane and 2% of nitrogen) needed for the process if the calorific value of methane is 890 310 kJ/kmole

Solution. According to the reaction equation

$$(CH_3)_2CO \rightarrow CH_2{=}CO \rightarrow (CH_3CO)_2O$$

the theoretical consumption of acetone is $58 \times 1000/102 = 568$ kg/h. As the yield of the process is 0.25 the actual consumption of acetone is $568/0.25 = 2270$ kg/h.

The heat supplied with acetone is

$$Q_1 = 2.09 \times 2270 \times 20 = 94\,886 \text{ kJ}$$

The heat used for evaporation of acetone is

$$Q_2 = 2270 \times 553.5 = 1\,256\,440 \text{ kJ}$$

The heat needed for the reaction is

$$Q_r = 568 \times 1000 \times 83.7/58 = 819\,683 \text{ kJ}$$

The heat removed with the gas mixture is

$$Q_3 = 2.26 \times 2270 \times 800 = 4\,104\,160 \text{ kJ}$$

The total consumption of heat is $1\,256\,440 + 819\,683 + 4\,104\,160 = 6\,180\,283$ kJ.

Hence, the amount of methane needed to supply the heat for the process is $(6\,180\,283 - 94\,886)/890\,310 = 6.84$ kmole. The respective amount of the natural gas is $6.84 \times 22.4/0.98 = 156.5$ m³. The heat balance of the process is summarized in Table 23.

TABLE 23

Inputs	kJ	%	Outputs	kJ	%
Q_1	94 886	1.53	Q_2	1 256 440	20.1
Q	6 085 397	98.47	Q_r	819 863	13.1
			Q_3	4 104 160	66.8
Total:	6 180 283	100.0	*Total*:	6 180 283	100.0

Problem 27. Calculate the heat balance of the reactor for producing hydrogen by catalytic conversion of methane (see Chapter II, Problem 8) for 1000 m³ of hydrogen. The heat losses to the environment amount to 6% of the total heat. The conversion reaction is described by the following equation:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 - 206\,200 \text{ kJ}$$

The composition of the starting mixture—CH_4: $H_2O = 1 : 2$. The initial temperature of the mixture is 105 °C, the temperature at the reaction zone is 900 °C. The specific heats (kJ/kmole K):

	CH_4	H_2O	CO	H_2
100 °C	36.72	33.29	28.97	29.10
900 °C	—	38.14	31.36	29.90

Solution. Table 24 gives the volumes of starting materials and reaction products for 1000 m³ of hydrogen.

TABLE 24

Inputs	m³	Outputs	m³
CH_4	333	CO	333
H_2O	667	H_2O	334
		H_2	1000
Total:	1000	*Total*:	1667

The heat brought with methane is

$$Q'_{CH_4} = 333 \times 36.72 \times 105/22.4 = 57\,318 \text{ kJ}$$

The heat brought with water is

$$Q'_{H_2O} = 667 \times 33.29 \times 105/22.4 = 104\,083 \text{ kJ}$$

The sum of these heats is 161 401 kJ.

The heats removed from the reactor with the reaction products at 900 °C are:

$$Q_{CO} = 333 \times 31.36 \times 900/22.4 = 419\,579 \text{ kJ}$$

$$Q_{H_2O} = 334 \times 900 \times 38.14/22.4 = 511\,825 \text{ kJ}$$

$$Q_{H_2} = 1000 \times 29.9 \times 900/22.4 = 1\,201\,339 \text{ kJ}$$

The total removed heat is 2 132 743 kJ.

The heat required for the reaction is

$$Q_r = 333 \times 206\,200/22.4 = 3\,065\,384 \text{ kJ}$$

The total theoretical consumption of heat is 5 198 127 kJ. The heat losses are

$$Q_l = 161\,401 \times 0.06 = 9684 \text{ kJ}$$

The heat balance of methane conversion is summarized in Table 25.

TABLE 25

The Heat Balance for Methane Conversion

Inputs	kJ	Outputs	kJ
Q'_{CH_4}	57 318	Q_{CO}	419 579
Q'_{H_2O}	104 083	Q_{H_2}	1 201 339
		Q_{H_2O}	511 825
		Q_l	9 684
		Q_r	3 065 384
Total:	161 401	*Total*:	5 207 811

Hence, the heat which should be supplied to the reaction zone is 5 207 811 — 161 401 = 5 046 410 kJ. Combustion of natural-gas methane is used to supply this heat (the gas contains 98% methane and 2% nitrogen):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 890\,950 \text{ kJ/kmole}$$

The required amount of methane is 5 046 410/890 950 = 5.66 kmole or 5.66 × 22.4 = 127 m³. The respective amount of natural gas is 127/0.98 = 129.5 m³.

Problem 28. Calculate the heat balance for water gas production per 1 ton of coke containing 93% (by mass) C, 4% (by mass) ash, and 3% (by mass) H_2O. The consumption of steam is 1575 kg per 1 ton of coke and the yield of water gas is 2190 kg. The gas contains 89.9% (by mass) CO, 1.94% (by mass) CO_2, and 8.16% (by mass) H_2. The temperature of the reaction products is 1000 °C, the steam is fed at 100 °C and the initial temperature of coke is 25 °C.

TABLE 26

Product	Molecular mass	*t*, °C	c, J/mole K
C	12	25	8.53
H_2O	18	100	33.2
CO	28	1000	31.7
H_2	2	1000	29.8
CO_2	44	1000	49.3

Solution. 2190 kg of gas contain 2190 × 0.899 = 1969 kg or 1969 × 22.4/28 = 1575 m³ of CO, 2190 × 0.0194= 42.5 kg or 42.4× × 22.4/44 = 21.6 m³ of CO_2, and 2190 × 0.0816 = 178.7 kg or 178.6 × 22.4/2 = 2000 m³ of H_2.

Assume that the specific heat of ash is the same as that of carbon. Then the heat supplied with carbon and ash of coke (93% C + + 4% ash = 97%) is

$$Q_1 = 1000 \times 0.97 \times 8.53 \times 25/12 = 17\,237 \text{ kJ}$$

The heat supplied with moisture of the coke is

$$Q_2 = 1000 \times 0.03 \times 4.187 \times 25 = 3140 \text{ kJ}$$

The heat supplied with steam is

$$Q_3 = 1575 \times 33.2 \times 100/18 = 290\,500 \text{ kJ}$$

Production of gas is described by the following equations:

$$C + H_2O \rightleftarrows CO + H_2 - q_1 \quad (1)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 + q_2 \quad (2)$$

The formation heats at 25 °C (kJ/kmole): CO_2—393 510, CO—110 500, H_2O (steam)—241 840. Hence, we find

$$q_1 = 110\,500 - 241\,840 = -131\,340 \text{ kJ}$$

and

$$q_2 = 393\,510 - (110\,500 + 241\,840) = 41\,170 \text{ kJ}$$

Thus, the consumption of heat in the endothermic reaction (1) is

$$Q_4 = 131\,340 \times 930/12 = 10\,178\,850 \text{ kJ}$$

The heat liberated in the exothermic reaction (2) is

$$Q_5 = 41\,170 \times 21.6/22.4 = 39\,700 \text{ kJ}$$

The total heat effect of reactions (1) and (2) is

$$Q_6 = Q_4 - Q_5 = 10\,139\,150 \text{ kJ}$$

The amount of heat removed with the reaction products: for CO_2—$49.3 \times 21.5 \times 1000/22.4 = 47\,539$ kJ, for CO $31.7 \times 1\,575 \times \times 1000/22.4 = 2\,228\,906$ kJ, and for H_2—$29.8 \times 2000 \times \times 1000/22.4 = 2\,660\,714$ kJ. The total removed heat is

$$Q_7 = 4\,937\,159 \text{ kJ}$$

Hence, the total amount of heat which must be delivered for the reaction is $Q_6 + Q_7 - (Q_1 + Q_2 + Q_3) = 14\,765\,432$ kJ. This heat is supplied by the exothermic reaction yielding the producer gas:

$$2C + O_2 = 2CO + 2 \times 110\,500 \text{ kJ}$$

The amount G_c of coke (93% C) needed to supply heat for the above process can be found from the following proportion:

$$12 \text{ kg} — 110\,500 \text{ kJ}$$

$$G_c \times 0.93 \text{ kg} — 14\,765\,432 \text{ kJ}$$

Hence, $G_c = \frac{14\,765\,432 \times 12}{110\,500 \times 0.93} = 172.4$ kg

The amount of oxygen needed for oxidizing this coke is $11.2 \times \times 172.4/12 = 1609$ m³. The respective amount of air is $1609 \times \times 100/21 = 7662$ m³ containing $1630 \times 3.76 = 6153$ m³ of nitrogen. Table 27 describes the heat balance of the process per 1 ton of coke.

Problem 29. Calculate the heat balance of the furnace for roasting pyrite using the table of material balance given in the solution of Problem 19, Chapter I. The temperature of the fluidized bed is 800 °C. The specific heats at 20 °C: for pyrite $c_{pyr} = 0.538$ kJ/kg K, $c_{a\,tr} = 4.187\ (0.308 + 0.00024T) = 1.3097$ kJ/m³ K = 1.0119 kJ/kg K, and $c_{H_2O} = 2.006$ kJ/m³ K.

TABLE 27

Inputs	kJ	%	Outputs	kJ	%
Q_1	17 237	0.115	Q_7	4 937 159	35.3
Q_2	3 140	0.015	Q_6	10 139 150	67.7
Q_3	290 500	1.97			
Heat of reaction					
$2C+O_2=2CO$	14 765 432	97.9			
Total:	15 076 309	100	*Total*:	15 076 309	100

The specific heats at 800 °C: for cinder $c_c = 0.883$ kJ/m³ K, $c_{SO_2} = 2.428$ kJ/m³ K, $c_{O_2} = 1.521$ kJ/m³ K, $c_{N_2} = 1.463$ kJ/m³ K, $c_{H_2O} = 1.884$ kJ/m³ K.

Solution. (1) The heat brought with dry pyrite is

$$Q_1 = G_{pyr}c_{pyr}t = 8084 \times 0.538 \times 20 = 86\,984 \text{ kJ}$$

(2) The heat of the water in pyrite is

$$Q_2 = G_w c_w t = 250 \times 20 \times 4.187 = 20\,935 \text{ kJ}$$

(3) The heat of dry air is

$$Q_3 = G_{air}c_{air}t = 17\,700 \times 1.3097 \times 20 = 463\,634 \text{ kJ}$$

or

$$22\,900 \times 1.0119 \times 20 = 463\,634 \text{ kJ}$$

(4) The heat of the air moisture is

$$Q_4 = 204 \times 2.008 \times 20 = 8\,184 \text{ kJ}$$

The exothermic reaction of pyrite roasting is described by the following equation:

$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3 + 3400 \text{ kJ}$$

The reaction equation shows that formation of 8 kmoles or 8×22.4 m³ of SO_2 results in liberation of 3400×10^3 kJ. Hence, when 2360 m³ of SO_2 are produced we have

$$Q_5 = 3400 \times 2360 \times 1000/8 \times 22.4 = 44\,776\,786 \text{ kJ}$$

The total input of heat is $Q_1 + Q_2 + Q_3 + Q_4 + Q_5 = 45\,356\,523$ kJ.

Now calculate the consumption of heat. (1) The heat removed with the cinder is

$$Q_6 = G_c c_c t = 6000 \times 800 \times 0.883 = 4\,238\,400 \text{ kJ}$$

(2) The heat removed with the roaster gas is

$$Q_7 = Q_{SO_2} + Q_{N_2} + Q_{O_2} + Q_{H_2O}$$

$$Q_{SO_2} = V_{SO_2} c_{SO_2} t = 2360 \times 2.428 \times 800 = 4\,584\,064 \text{ kJ}$$

$$Q_{N_2} = 12\,900 \times 1.463 \times 800 = 15\,098\,160 \text{ kJ}$$

$$Q_{O_2} = 400 \times 1.571 \times 800 = 502\,720 \text{ kJ}$$

$$Q_{H_2O} = 516 \times 1.884 \times 800 = 777\,715 \text{ kJ}$$

Hence, $Q_7 = 20\,962\,659$ kJ

(3) The heat losses to the environment (which in practice amount to 2-5% of the total heat input) are assumed to be 4%. Then the heat losses are

$$Q_8 = 0.04 \times 45\,356\,523 = 1\,814\,261 \text{ kJ}$$

(4) The heat utilized for steam production in the tubes of the waste-heat boiler in the fluidized bed which is

$$Q_9 = Q_1 + Q_2 + Q_3 + Q_4 + Q_5 - (Q_6 + Q_7 + Q_8) = 18\,341\,203 \text{ kJ}$$

Removal of this heat makes it possible to maintain the constant temperature of 800 °C in the fluidized bed.

The amount of steam produced per hour is $Q_9/i = 18\,341\,203/3210 = 5\,714$ kg (here $i = 3210$ kJ/kg is the enthalpy of the steam at 400°C and 40×10^5 Pa). Table 28 presents the results of the heat balance calculations.

TABLE 28

Inputs	kJ	%	Outputs	kJ	%
Q_1	86 984	0.19	Q_6	4 238 400	9.34
Q_2	20 935	0.05	Q_7	20 962 659	46.22
Q_3	463 634	1.02	Q_8	1 814 261	4.0
Q_4	8 184	0.02	Q_9	18 341 203	40.44
Q_5	44 776 786	98.77			
Total:	45 356 523 ≈	100.0	*Total*:	45 356 523	100.0

Problem 30. Thermoxidative cracking of the natural gas containing 98% CH_4, 0.5% CO_2, and 1.5% N_2 yields the final mixture containing 9% C_2H_2, 26% CO, 54% H_2, 0.5% C_2H_4, 4.5% CO_2, and 6% CH_4. The process involves the following reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 890\,310 \text{ kJ/kmole} \quad (1)$$

$$CH_4 + 1.5O_2 = CO + 2H_2O + 687\,000 \text{ kJ/kmole} \quad (2)$$

$$CH_4 + 0.5O_2 = CO + 2H_2 + 35\,650 \text{ kJ/kmole} \quad (3)$$

$$H_2 + 0.5O_2 = H_2O + 285\,840 \text{ kJ/kmole} \quad (4)$$

$$2CH_4 = C_2H_2 + 3H_2 - 376\,450 \text{ kJ/kmole} \quad (5)$$

$$2CH_4 = C_2H_4 + 2H_2 - 201\,980 \text{ kJ/kmole} \quad (6)$$

The following proportions of methane are converted in the reactions: reaction (1)—11.6%, reaction (2)—42.4%, and reaction (3)—46%.

Methane and commercial-grade oxygen containing 1% nitrogen are fed to the apparatus at 800 °C. The final mixture has the temperature of 1500 °C, that is, the cracking temperature.

Calculate the heat balance per 1 ton of acetylene and the required amount of natural gas.

Solution. Calculate the amount of methane which is needed to produce 1 ton of C_2H_2 in reaction (5):

$$V_{C_2H_2} = 1000 \times 22.4/26 = 862 \text{ m}^3$$

(26 is the molecular mass of acetylene). The volume of the final gas mixture is 862/0.09 = 9600 m³.

Methane amount, m³	
Reaction (1)	337
Reaction (2)	1200
Reaction (3)	1300
Reaction (5)	1724
Reaction (6)	96
Unreacted	673
Total:	5330

The amount of natural gas containing 5330 m³ of methane is 5330/0.98 = 5450 m³. This amount of gas contains 28 m³ of CO_2 and 85 m³ of N_2.

Oxygen amount, m³	
Reaction (1)	$337 \times 2 = 674$
Reaction (2)	$1200 \times 1.5 = 1800$
Reaction (3)	$1300 \times 0.5 = 650$
Reaction (4)	$102 \times 0.5 = 51$
Total:	3175

The amount of nitrogen supplied with the oxygen is 3175 × × 0.01/0.99=32 m³. The amount of hydrogen liberated in the reactions: (3)—2600 m³, (5)—2586 m³, (6)—96 m³, the total—5282 m³. Out of that amount 102 m³ are burned in reaction (4). The amount of steam liberated in the reactions: (1)—674 m³, (2)—2400 m³, (4)—102 m³, the total—3176 m³.

Table 29 gives the composition of the gas and the specific heats of the components.

TABLE 29

INPUTS				OUTPUTS		
Gas	V(m³)	t (°C)	c (kJ/kmole K)	V (m³)	t (°C)	c (kJ/kmole K)
CH_4	5330	800	55.8	673	1500	69.5
O_2	3175	800	32.3	—	—	—
N_2	32+85	800	30.8	117	1500	32.4
CO_2	28	800	47.5	365	1500	52.6
CO	—	—	—	2500	1500	32.9
H_2	—	—	—	5180	1500	30.6
C_2H_2	—	—	—	862	1500	66.0
C_2H_4	—	—	—	48	1500	94.6
H_2O (steam)	—	—	—	3176	1500	41.2
Total:	8650			12 921		

The amounts of heat delivered to the apparatus with materials: $Q_{CH_4} = 5330 \times 55.8 \times 800/22.4 = 6\,490\,000$ kJ, $Q_{O_2} = 3175 \times \times 32.3 \times 800/22.4 = 3\,660\,000$ kJ, $Q_{N_2} = 117 \times 30.8 \times 800/22.4 = = 128\,000$ kJ, $Q_{CO_2} = 28 \times 47.5 \times 800/22.4 = 47\,500$ kJ, the total—$Q_{del} = 10\,326\,300$ kJ.

The heats liberated in the exothermic reactions: $Q_1 = 337 \times \times 890\,310/22.4 = 13\,400\,000$ kJ, $Q_2 = 1200 \times 687\,000/22.4 = = 36\,800\,000$ kJ, $Q_3 = 1300 \times 35\,650/22.4 = 2\,070\,000$ kJ, $Q_4 = = 102 \times 285\,840/22.4 = 1\,300\,000$ kJ, the total—53 570 000 kJ.

The heats removed with the reaction products: $Q_{CH_4} = 673 \times \times 69.5 \times 1500/22.4 = 3\,126\,000$ kJ, $Q_{H_2} = 5180 \times 30.6 \times \times 1500/22.4 = 10\,600\,000$ kJ, $Q_{CO} = 2500 \times 32.9 \times 1500/22.4 = = 5\,500\,000$ kJ, $Q_{CO_2} = 365 \times 52.6 \times 1500/22.4 = 1\,280\,000$ kJ, $Q_{C_2H_2} = 862 \times 66.0 \times 1500/22.4 = 3\,760\,000$ kJ, $Q_{C_2H_4} = 48 \times \times 94.6 \times 1500/22.4 = 340\,000$ kJ, $Q_{N_2} = 117 \times 32.4 \times \times 1500/22.4 = 254\,000$ kJ, $Q_{steam} = 3176 \times 41.2 \times 1500/22.4 = = 8\,750\,000$ kJ, the total—33 610 000 kJ.

The heats consumed in the endothermic reactions: $Q_5 = 1724 \times \times 376\,450/22.4 = 29\,000\,000$ kJ, $Q_6 = 96 \times 201\,980/22.4 = = 860\,000$ kJ, the total—29 860 000 kJ.

Table 30 presents the heat balance for production of 1 ton of acetylene.

TABLE 30

INPUTS	kJ	%	OUTPUTS	kJ	%
Q_{del}	10 326 300	16.1	Q_{rem}	33 610 000	52.6
Q_r	53 570 000	83.9	Q_r	29 860 000	47.4
Total:	63 896 300	100.0	*Total*:	63 470 000	100.0

The discrepancy of the heat balance is (63 896 300 — 63 470 000) × × 100/63 896 300 = 0.67%. As recommended, the process is conducted with a small heat excess.

Problem 31. Calculate the heat balance of the reactor for oxidation of methanol into formaldehyde in the fluidized catalyst bed. Find the areas of the cooling surfaces of the coil cooler for cooling the catalyst bed and of the cooler for quenching the reaction products.

The material balance for the process see in Chapter I, Problem 20. The temperature in the fluidized bed is 600 °C, the air-methanol mixture is fed into the reactor at 70 °C. The temperature of the quenched reaction products is 200 °C. The water temperature in the coolers is 20 °C at entry and 50 °C at exit. The heat transfer coefficient between the cooling water and the fluidized bed is 380 W/m² K. The heat transfer coefficient between the reaction products and the second cooler is 290 W/m² K. The heat losses in the reactor amount to 5% of the total heat input.

Solution. The heat inputs to the reactor consist of the heats Q_1 of reactions of methanol oxidation and the heat Q_2 delivered by the air-methanol mixture. The heat outputs comprise the heat Q_3 of the reaction products leaving the reactor, the heat losses Q_4 in the reactor and the heat Q_5 removed by the cooling water from the reactor. The heat Q_5 is given by the heat balance equation

$$Q_5 = Q_1 + Q_2 - (Q_3 + Q_4)$$

Heat inputs. Calculate the heat effects of the reactions of methanol oxidation (per 1 hour of operation of the reactor). Using the material balance data draw up the stoichiometric equation of catalytic oxidation of methanol. The amount of methanol oxidized in the main and side reactions is 58.1 — 11.6 = 46.5 kmoles and the respective amount of oxygen is 18.26 kmoles. The equation is:

$$46.5\ CH_3OH + 18.26\ O_2 = 40.7\ CH_2O + 31.78\ H_2O + 2.75\ HCOOH + + 2.45\ CO_2 + 0.15\ CO + 0.46\ CH_4 + 16.85\ H_2$$

The heat Q_1 can be found from the Hess law using the formation heats for the compounds. From the reaction equation we obtain for the reaction products at the temperature 25 °C = 298 K: CH_2O—

40.7 × 115 900 = 4 716 000 kJ, H_2O—31.78 × 241 840 = = 7 685 700 kJ, HCOOH—2.75 × 376 700 = 1 035 900 kJ, CO_2— 2.45 × 393 510 = 964 100 kJ, CO—0.15 × 110 500 = 16 900 kJ, CH_4—0.46 × 74 850 = 34 400 kJ, the sum of the terms of the right-hand side of the equation is 14 453 000 kJ, CH_3OH—46.5×201 200 = = 9 355 800 kJ. Hence, Q_1 = 14 453 000 — 9 355 800 = = 5 097 200 kJ at 298 K. Let us find the heat effect of these reactions at the temperature of the process (600 °C = 873 K). The temperature dependence of the heat effect of a reaction is given by the following equation:

$$Q_T = Q_{298} + \int_{298}^{873} \sum \nu c'_p - \sum \nu c''_p$$

Here c'_p is the molecular heat of a reactant, c''_p is the molecular heat of a reaction product, and ν is the number of moles of each component.

The temperature variation of the molecular heat can be approximated by the equation $c_p = a + bT + cT^2$. Substituting this equation into the equation for Q_T and integrating it we obtain

$$Q_T = Q_{298} + \alpha (T - 298) + \beta (T^2 - 298^2) + \gamma (T^3 - 298^3)$$

Here $\alpha = \Sigma \nu a$, $\beta = 1/2\ \Sigma \nu b$, and $\gamma = 1/3 \Sigma \nu c$.

To find the factors α, β, and γ write down the temperature dependences of the molecular heats for the components (in kJ/kmole K):

$$c_{p\,CH_3OH} = 20.45 + 0.1037T - 0.0247 \times 10^{-3} T^2$$
$$c_{p\,CH_2O} = 20.94 + 0.0586T - 0.0156 \times 10^{-3} T^2$$
$$c_{p\,H_2O} = 28.8 + 0.01375T - 1.435 \times 10^{-6} T^2$$
$$c_{p\,HCOOH} = 30.7 + 0.0895T - 0.0346 \times 10^{-3} T^2$$
$$c_{p\,CO_2} = 32.2 + 0.0222T - 3.48 \times 10^{-6} T^2$$
$$c_{p\,CO} = 26.2 + 0.00875T - 1.92 \times 10^{-6} T^2$$
$$c_{p\,CH_4} = 14.15 + 0.075T - 17.54 \times 10^{-6} T^2$$
$$c_{p\,O_2} = 26.2 + 0.0115T - 3.22 \times 10^{-6} T^2$$
$$c_{p\,H_2} = 28.8 + 0.000276T + 1.17 \times 10^{-6} T^2$$

Hence we obtain $\alpha = \Sigma \nu a = (46.5 \times 20.45 + 18.26 \times 26.2) -$ $- (40.7 \times 20.94 + 31.78 \times 28.8 + 16.85 \times 28.8 + 2.75 \times 30.7 +$ $+ 2.45 \times 32.2 + 0.15 \times 26.2 + 0.46 \times 14.15) = -999.5$; $\beta = 1/2 \Sigma \nu b = 1/2\ [(46.5 \times 0.104 + 18.26 \times 0.0115) - (40.7 \times$ $\times 0.0586 + 31.78 \times 0.01375 + 16.85 \times 0.000276 + 2.75 \times$ $\times 0.0895 + 2.45 \times 0.0222 + 0.15 \times 0.00875 + 0.46 \times 0.075)] =$

$= 0.942$; $\gamma = 1/3\ \Sigma\nu c = 1/3\ [(-46.5 \times 24.7 - 18.75 \times 3.22) - (40.7 \times 15.6 - 31.78 \times 1.435 + 16.85 \times 1.17 - 2.75 \times 34.6 - 2.45 \times 3.48 - 0.15 \times 1.92 - 0.46 \times 17.54)\ 10^{-6}] = -144.2 \times 10^{-6}$.

Thus, the total heat of the process at 600 °C is

$$Q_1 = 5\,097\,200 - 999.5 \times 575 + 0.942\,(873^2 - 298^2) - 144.2 \times 10^{-6}\,(873^3 - 298^3) = 5\,064\,466 \text{ kJ}$$

The difference between the heats of the process at 25 and 600 °C is only 32 740 kJ or 0.64% so that in approximate calculations we can ignore it and use the value for 25 °C.

To find the heat Q_2 brought by the air-methanol mixture at 70 °C (343 K) we should find the specific heats for the components of the mixture from the above formulas.

$$c_{p\text{CH}_3\text{OH}} = 20.45 + 0.1037 \times 343 - 0.0247 \times 10^{-3} \times 343^2 = 53.2 \text{ kJ/kmole K}$$

$$c_{p\text{O}_2} = 26.2 + 0.0115 \times 343 - 3.22 \times 10^{-6} \times 343^2 = 29.76 \text{ kJ/kmole K}$$

$$c_{p\text{N}_2} = 26.4 + 0.0076 \times 343 - 1.445 \times 10^{-6} \times 343^2 = 28.83 \text{ kJ/kmole K}$$

The heats brought by the mixture components:

$$Q_{\text{CH}_3\text{OH}} = 216\,000 \text{ kJ}; \quad Q_{\text{O}_2} = 38\,000 \text{ kJ};$$

$$Q_{\text{N}_2} = 139\,000 \text{ kJ}; \quad Q_2 = 393\,000 \text{ kJ}.$$

The total input of heat is

$$Q_{\text{in}} = Q_1 + Q_2 = 5\,457\,466 \text{ kJ}$$

Heat outputs. The heat Q_3 removed by the reaction products at 600 °C is the sum of heats of individual products (specific heats are taken from the handbooks): $Q_{\text{CH}_2\text{O}} = 40.7 \times 47.3 \times 600 = 1\,166\,800$ kJ; $Q_{\text{CH}_3\text{OH}} = 11.6 \times 74.2 \times 600 = 517\,300$ kJ; $Q_{\text{HCOOH}} = 2.75 \times 70.7 \times 600 = 116\,500$ kJ; $Q_{\text{CO}_2} = 2.45 \times 45.5 \times 600 = 66\,900$ kJ; $Q_{\text{H}_2\text{O}} = 31.78 \times 36.2 \times 600 = 690\,900$ kJ; $Q_{\text{CO}} = 0.15 \times 30.5 \times 600 = 2800$ kJ; $Q_{\text{CH}_4} = 0.46 \times 50.9 \times 600 = 14\,000$ kJ; $Q_{\text{H}_2} = 16.85 \times 29.4 \times 600 = 297\,100$ kJ; $Q_{\text{N}_2} = 68.73 \times 30.2 \times 600 = 1\,247\,400$ kJ; and $Q_3 = 4\,119\,700$ kJ.

The heat losses Q_4 are 5% of the total heat input: $Q_4 = 5\,457\,466 \times 0.05 = 272\,873$ kJ.

The amount of heat Q_5 which should be removed from the fluidized bed can be found from the heat balance equation:

$$Q_5 = Q_1 + Q_2 - (Q_3 + Q_4) = 1\,064\,893 \text{ kJ}$$

Table 31 describes the heat balance of the process.

To find the area of the heat exchange surface F_1 for the first cooler assume isothermal conditions and find the mean temperature dif-

TABLE 31

INPUTS	kJ	OUTPUTS	kJ
Q_1	5 064 466	Q_3	4 119 700
Q_2	393 000	Q_4	272 873
		Q_5	1 064 893
Total:	5 457 466	*Total:*	5 457 466

ference

$$\Delta t_1 = [(600 - 20) + (600 - 50)]/2 = 565 \text{ K}$$

Hence, we obtain

$$F_1 = 1\ 064\ 893 \times 10^3/565 \times 380 \times 3600 = 1.38 \text{ m}^2$$

To find the area F_2 of the heat exchange surface of the second cooler we should find the heat of the reaction products at 200 °C. Using the specific heat values from the handbooks we find $Q_{CH_2O} = 40.7 \times \times 39.6 \times 200 = 322\ 260$ kJ; $Q_{CH_3OH} = 11.6 \times 57 \times 200 = = 132\ 470$; $Q_{H_2O} = 31.78 \times 6760 = 214\ 830$ kJ; $Q_{H_2} = 16.85 \times \times 5820 = 98\ 067$ kJ; $Q_{HCOOH} = 2.75 \times 7.6 \times 200 = 4180$ kJ; $Q_{CO_2} = 2.45 \times 2120 = 5194$ kJ; $Q_{CO} = 0.15 \times 5840 = 890$ kJ; $Q_{CH_4} = 0.46 \times 7940 = 3640$ kJ; $Q_{N_2} = 68.73 \times 5800 = 390\ 630$ kJ; the total is 1 172 161 kJ. Hence, the heat which should be removed from the reaction products is $Q_6 = 4\ 119\ 700 - - 1\ 216\ 600 = 2\ 947\ 539$ kJ.

The mean temperature difference between the reaction products and the cooling water is

$$\Delta t_2 = [(200 - 20) + (200 - 50)]/2 = 165 \text{ K}$$

The cooling surface area is

$$F_2 = 2\ 947\ 539 \times 10^3/290 \times 165 \times 3600 = 17.1 \text{ m}^2$$

The cooler is placed at the top of the reactor and consists of a water jacket and coils.

Further Problems for Students

1. Calculate the heat effect of ethylene conversion (in kJ/mole):

$$C_2H_4 + 2H_2O \rightleftharpoons 2CO + 4H_2 + Q$$

2. Calculate the theoretical temperature of propane combustion with the air excess of 20%. The reaction is described by the equation

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + Q$$

3. Calculate the calorific value of the coke-oven gas containing 59% H_2, 24% CH_4, 2% C_2H_4, 6% CO, 2.8% CO_2, 0.6% O_2, and 5.6% N_2.

4. Calculate the theoretical temperature of sulphur combustion in the air according to the reaction

$$S + O_2 + 3.76N_2 \rightarrow SO_2 + 3.76N_2 + Q$$

5. Calculate the highest and the lowest combustion heats and the theoretical consumption of air for combustion of the peat containing 58% C, 6% H_2, 31% O_2, 0.1% S, 1.9% N_2, 2% H_2O, and 1% ash.

6. Calculate the temperature of combustion for the anthracite containing 91.5% C, 1.8% H_2, 1.7% O_2, 1.5% S, 1% N_2, 2% H_2O, and 0.5% ash and find the composition of the reaction products for the air excess ratio of 1.4.

7. Find the composition of the combustion products and the heat effect for combustion of the natural gas containing 93.0% CH_4, 4.5% C_2H_6, 1.9% C_3H_8, 0.1% CO_2, and 0.5% N_2. The theoretically required amount of air is used.

8. Calculate the heat balance of the one-stage conversion of methane at 1000 °C for 1000 m^3 of H_2. The equation reaction is

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 - Q$$

9. Calculate the heat balance for reduction of 1 ton of nitrobenzene with iron chips. The degree of reduction is 92%. The apparatus is charged with 120 kg of iron chips, 20 kg of HCl, and 290 kg of 3% aniline solution at 20 °C. Then the mixture is heated with live steam to 100 °C and 1.1% of the stoichiometric amount of nitrobenzene is added. The temperature of the process is self-maintained at 100 °C.

10. Find the heat effect of the neutralization reaction

$$H_2SO_4 + 2NH_3 \rightleftarrows (NH_4)_2SO_4 + Q$$

for the 75% acid. Calculate the amount of water which can be evaporated at the expense of the liberated heat.

11. Calculate the heat liberated upon mixing of 10 kg of 98.5% H_2SO_4 with 5 kg of 20% sulphuric acid.

12. Gaseous ammonia is passed through 50% HNO_3 at 20 °C. Find the heat effect of the neutralization reaction and the temperature of the final reaction mixture. The heat losses amount to 15% of the liberated heat.

Part Two

Elementary Calculations of Chemical Reactors

Chapter IV

Kinetics of Chemical Technological Processes

Introduction

Fundamental equations for process rates. Any chemical technological process can be described as consisting of the following interrelated stages: (1) delivery of the reacting components to the reaction zone; (2) chemical reactions; and (3) removal of the reaction products from the reaction zone.

Figure 1 presents a typical schematic diagram for the chemical technological process.

An industrial chemist who has to design a reactor for a chemical technological process must know, first of all, the kinetics of the pro-

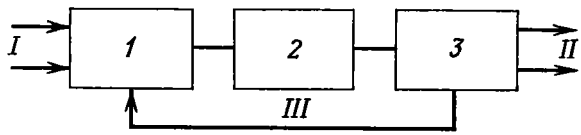


Fig. 1. Schematic diagram of a typical chemical technological process: *1* and *3*—physical operations; *2*—chemical transformations; *I*—starting materials; *II*—products; *III*—recycled components.

cess. The rate of the process determines the capacity of the reactors and the productivity and the intensity of operation of the plant. The knowledge of the effects of various factors on the process rate makes possible planned control of the process and application of special measures to reach the maximum yields of the products in the shortest possible time.

The total rate of the process depends on the rates of individual stages of the process and is determined by the slowest (limiting) stage. If the slowest stage is the delivery of the reactants to the reaction zone or removal of the reaction products and it limits the total rate of the process the latter is referred to as being the *diffusion-limited* one. If the total rate of the process is limited by the rates of the chemical reactions or one of them the process is known as a *kinetics limited* one. If the rates of all the stages are comparable the process is said to be an *intermediate* one.

Depending on the region of the process different equations can be used to describe mathematically the process rate and different methods can be applied to increase the total rate of the process.

In the general case the rate of a chemical process can be assumed to be proportional to the driving force of the process:

$$u = k \Delta C \qquad \text{(IV.1)}$$

Here u is the process rate, k is the proportionality factor, and ΔC is the driving force of the process.

The factor k characterizes the process rate and is known as the process rate constant. The constant k, typically, reflects the effects of all the factors which are not involved in the driving force as well as all the deviations of the real process from the simplified description.

We shall analyse separately the features of the kinetics- and diffusion-limited processes. This chapter deals with the kinetics-limited processes. The kinetics of the diffusion-limited processes is discussed below in Chapter VII.

The reaction rate can be expressed as variation of the number of moles of a component per unit time in the unit volume of the phase (for homogeneous reaction) or on the unit area of the phase interface (for heterogeneous reaction).

This definition yields Eq. (IV.2) for the reaction rate of the homogeneous reaction and Eq. (IV.3) for the heterogeneous reaction:

$$u = \pm \frac{1}{v} \frac{dN}{d\tau} \qquad \text{(IV.2)}$$

$$u = \pm \frac{1}{F} \frac{dN}{d\tau} \qquad \text{(IV.3)}$$

Here N is the number of moles of the component which were formed or reacted, v is the volume of the reaction zone, F is the area of the interface between the phases, τ is the time.

The reaction rate can be expressed in other ways. For instance, if the volume of the reaction zone is the volume of the reactor $v = v_r = \text{const}$ we have

$$u = \pm \frac{1}{v_r} \frac{dN}{d\tau} \qquad \text{(IV.4)}$$

and

$$u = \pm \frac{d(N/v_r)}{d\tau} = \pm \frac{dC}{d\tau} \qquad \text{(IV.4a)}$$

The volume v can also be replaced by the mass G:

$$u = \pm \frac{1}{G} \frac{dN}{d\tau} \qquad \text{(IV.5)}$$

For the homogeneous systems v and v_r are, typically, identical and Eqs. (IV.2) and (IV.4) are identical, too. The reaction rate depends on the parameters of the system. This dependence does not change when the expression of the reaction rate is changed; only the proportionality factors and their dimensions are altered.

The reaction rate is proportional to the product of concentrations of the reactants raised to certain powers. For instance, for the model irreversible reaction $aA + bB \rightarrow dD$

$$u = k[A]^{\alpha}[B]^{\beta} \qquad \text{(IV.6)}$$

where k is the reaction rate constant which depends only on the temperature. The exponents α and β determine the order of the reaction. The reaction order can be measured experimentally. To predict the reaction order the mechanism of the reaction should be understood. Typically, the exponents α and β differ from the stoichiometric factors a and b which reflect the molecularity of the reaction. But if the stoichiometric equation correctly describes the mechanism of the reaction the order of the reaction is the same as its molecularity, that is, the first-order reaction is monomolecular, the second-order reaction is bimolecular, and so on. The rates of conversion of the components involved in the reaction are interrelated through the stoichiometric factors. For instance, for the reaction described by the stoichiometric equation $A + B \rightarrow 2D$ the relationship between the rates of conversion of the components can be written as

$$\frac{dC_D}{d\tau} = -\frac{2dC_A}{d\tau} = -\frac{2dC_B}{d\tau} \qquad \text{(IV.7)}$$

That means that the rate of increase of the concentration of the component D is twice the rate of consumption of the components A and B. Therefore it is always necessary to specify for which component the reaction rate has been found as this will determine the calculated value of the reaction rate constant.

Let us analyse some essentially different equations for the reaction rates.

The irreversible reaction $aA + bB \rightarrow dD$:

$$u_D = k[A]^{\alpha}[B]^{\beta} \qquad \text{(IV.8)}$$

The reversible reaction $aA + bB \rightleftarrows dD$:

$$u_D = k_1 [A]^{\alpha} [B]^{\beta} - k_2 [D]^{\gamma} \qquad (IV.9)$$

In the general form we can write

$$u_D = k_1 [A]^{\alpha} [B]^{\beta} [D]^{\gamma} - k_2 [A]^{\alpha'} [B]^{\beta'} [D]^{\gamma'} \qquad (IV.10)$$

that is, the rates of the direct reaction and the reverse reaction depend on the concentrations of all the components involved in the reaction. This yields a practically useful relationship between the equilibrium constant and the constants of the direct and reverse reactions. For instance, for the above reaction at equilibrium

$$\frac{k_1}{k_2} = \frac{[D]_e^{\gamma'-\gamma}}{[A]_e^{\alpha-\alpha'} [B]_e^{\beta-\beta'}} \qquad (IV.11)$$

and the equilibrium constant is

$$K = \frac{[D]_e^d}{[A]_e^a [B]_e^b} \qquad (IV.12)$$

The ratio k_1/k_2 in Eq. (IV.11) can be regarded as a function of K:

$$k_1/k_2 = K^n \qquad (IV.13)$$

that is

$$\frac{[D]_e^{\gamma'-\gamma}}{[A]_e^{\alpha-\alpha'} [B]_e^{\beta-\beta'}} = \frac{[D]_e^{dn}}{[A]_e^{an} [B]_e^{bn}} \qquad (IV.14)$$

and

$$n = \frac{\alpha-\alpha'}{a} = \frac{\beta-\beta'}{b} = \frac{\gamma'-\gamma}{d} \qquad (IV.15)$$

For instance, synthesis of ammonia is described by the reaction

$$3H_2 + N_2 \rightleftarrows 2NH_3$$

with the equilibrium constant

$$K = \frac{[NH_3]^2}{[H_2]^3 [N_2]} \qquad (IV.16)$$

The reaction rate determined by M. Temkin and V. Pyzhev is

$$u = k_1 [N_2]^1 [H_2]^{1.5} [NH_3]^{-1} - k_2 [NH_3]^1 [H_2]^{-1.5} \qquad (IV.17)$$

here we have

$$n = \frac{1-0}{1} = \frac{1.5-(-1.5)}{3} = \frac{1+1}{2} = 1$$

Formation of nitric acid can be described by the following stoichiometric equation:

$$3N_2O_4 + 2H_2O \rightleftarrows 4HNO_3 + 2NO$$

For the constant concentration of nitric acid the reaction rate* is

$$u = k_1 [N_2O_4]^1 - k_2 [N_2O_4]^{1/4} [NO]^{1/2} \qquad (IV.18)$$

In this case we have $n = (1 - 1/4)/3 = (1/2 - 0)/2 = 1/4$, that is, $k_1/k_2 = K^{1/4}$.

Simultaneous and consecutive reactions. If both simultaneous reactions A + B → C and A + B → D are of the first order with respect to both reactants A and B we can write

$$\begin{aligned} u_C &= k_1 [A] [B] \\ u_D &= k_2 [A] [B] \\ u_A &= u_B = k_1 [A] [B] + k_2 [A] [B] \end{aligned} \qquad (IV.19)$$

Similar equations are valid for the consecutive reactions A + + B → C and A + C → D.

If we assume that both reactions are of the first order with respect to all components we can determine the reaction rate for each component:

$$\begin{aligned} u_B &= k_1 [A] [B] \\ u_D &= k_2 [A] [C] \\ u_A &= k_1 [A] [B] + k_2 [A] [C] \\ u_C &= k_1 [A] [B] - k_2 [A] [C] \end{aligned} \qquad (IV.20)$$

The equations show that the rate of consumption of A is the sum of the rates in the first and the second reaction while the rate of formation of C is, at first, positive, then it can vanish and, finally, it can become negative since the rate of the second reaction can be higher than that of the first. Hence, the concentration of C passes a maximum and then goes to zero.

It should be noted that Eqs. (IV.8), (IV.9), (IV.17)-(IV.20) involve instantaneous concentrations which may continuously vary. In calculations the instantaneous concentrations are replaced by the initial concentrations and the degrees of conversion by the moment τ or the initial numbers of moles (a, b, c and d) and the numbers of converted moles. Let us illustrate the above theory by the analysis of a first-order reaction carried out in a plug-flow or batch reactor: A → D. The rate of reaction is

$$u = -\frac{1}{v}\frac{dN_A}{d\tau} = k\left[\frac{N_A}{v}\right] \qquad (IV.21)$$

If v = const we have

$$u = -\frac{dC_A}{d\tau} = kC_A \qquad (IV.22)$$

* Denbigh K. G., Prince A. I. *J. Chem. Soc.*, 1947, p. 790.

If the instantaneous concentration C_A is expressed in terms of the initial number a of moles and the number X_M of reacted moles Eq. (IV. 22) is transformed into

$$-\frac{d(a-X_M)}{d\tau}=k(a-X_M) \quad \text{and} \quad \frac{dX_M}{d\tau}=k(a-X_M) \quad \text{(IV.22a)}$$

Integration of Eq. (IV.22a) yields

$$\frac{dX_M}{a-X_M}=k\,d\tau$$

$$k\int_0^{\tau} d\tau=\int_0^{X_M}\frac{dX_M}{a-X_M}=\left|-\ln(a-X_M)\right|_0^{X_M}=\ln\frac{a}{a-X_M}=k\tau$$

$$X_M=a(1-e^{-k\tau}) \quad \text{(IV.23)}$$

If the experimental results show that at the moment τ_1 $X_M = X_1$ and at the moment τ_2 $X_M = X_2$ the rate constant of the reaction can be found from the following equation:

$$k=\frac{2.3}{\tau_2-\tau_1}\log\frac{a-X_1}{a-X_2} \quad \text{(IV.24)}$$

The half-life of the reaction, that is, the period in which the concentrations of the reactants decrease by half, is

$$\tau_{1/2}=\frac{2.3}{k}\log 2=\frac{0.6932}{k} \quad \text{(IV.25)}$$

Similar equations can be derived for reactions of other orders.

The effect of temperature on reaction rates. To determine the optimum conditions for a chemical process we should analyse the effect of temperature on reaction rates for (1) irreversible processes and (2) reversible processes.

In the first case the temperature affects only the rate of the process while in the second case it affects both the rate and the equilibrium of the process.

Irreversible reaction. The kinetic equation describing the mechanism of the reaction $mA + nB \rightarrow pD$ can be written as

$$u=k[A]^m[B]^n \quad \text{(IV.26)}$$

The temperature dependence of the reaction rate constant is given by the Arrhenius equation

$$k=k_0e^{-E/RT} \quad \text{(IV.27)}$$

where E is the activation energy (kJ/kmole, kcal/kmole), R is the gas constant and k_0 is a constant.

Using Eq. (IV.27) we can find the reaction rate constants for a given temperature range if we know k_1 at T_1 or find the activation

energy E from the known k_1 and k_2 at T_1 and T_2 making the following transformations:

$$k_1/k_2 = k_0 e^{-E/RT_1}/k_0 e^{-E/RT_2} = e^{(E/R)(1/T_2 - 1/T_1)} \quad \text{(IV.28)}$$

$$\ln (k_1/k_2) = (E/R)(1/T_2 - 1/T_1) \quad \text{(IV.29)}$$

$$E = \frac{19.1 T_1 T_2}{T_1 - T_2} \log \frac{k_1}{k_2} \quad \text{(IV.30)}$$

According to Eqs. (IV.26) and (IV.27) the reaction rate constant and, hence, the reaction rate increase with increasing temperature. However, in the process of reaction the driving force $[A]^m[B]^n$ of the process decreases approaching zero at the end of the reaction, while the yield of the process approaches the maximum. This is illustrated by the plots in Fig. 2 which show that a longer time of reaction at a given temperature provides for a higher yield of the reaction.

Reversible reaction. The effect of temperature on the rates of reversible reactions is illustrated by the plots shown in Figs. 3 and 4.

Figure 3 shows that for the exothermic reactions the reaction yield as a function of temperature at a constant reaction time increases to a maximum and then decreases with increasing temperature. The temperature corresponding to the maximum reaction yield is known as the optimum temperature.

To find the maximum on the plot of the reaction yield as a function of temperature we can use the conventional calculus procedure, that is, find the point at which the first derivative is zero and the second derivative is negative.

Let us find the optimum temperature for the reversible exothermic reaction $aA + bB \rightleftarrows dD$ with the rate given by Eq. (IV.10)

$$u = k_1 [A]^\alpha [B]^\beta [D]^\nu - k_2 [D]^{\nu'} [A]^{\alpha'} [B]^{\beta'}$$

Equate the first derivative of u with respect to T to zero:

$$du/dT = \frac{dk_1}{dT} [A]^\alpha [B]^\beta [D]^\nu - \frac{dk_2}{dT} [A]^{\alpha'} [B]^{\beta'} [D]^{\nu'} = 0$$

$$\frac{dk_1}{dT} [A]^\alpha [B]^\beta [D]^\nu = \frac{dk_2}{dT} [A]^{\alpha'} [B]^{\beta'} [D]^{\nu'}$$

We have

$$\frac{dk}{dT} = k \frac{d \ln k}{dT}$$

and from Eq. (IV.27) we obtain

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

Hence we can write

$$\frac{E_1 k_1}{RT^2} [A]^\alpha [B]^\beta [D]^\nu = \frac{E_2 k_2}{RT^2} [A]^{\alpha'} [B]^{\beta'} [D]^{\nu'}$$

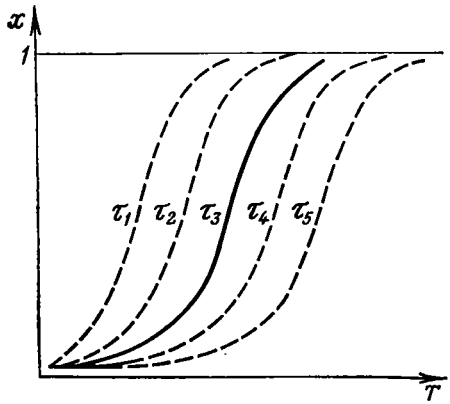


Fig. 2. The degree of conversion as a function of temperature in irreversible reactions. $\tau_1 > \tau_2 > \tau_3 > \tau_4 > \tau_5$.

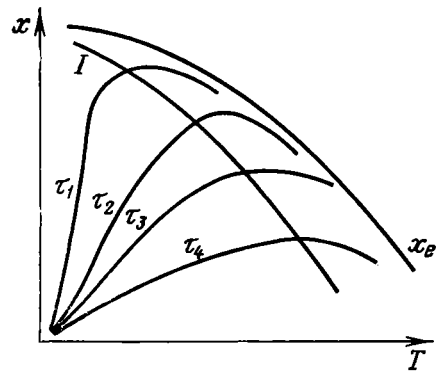


Fig. 3. The degree of conversion as a function of temperature in reversible exothermic reactions. $\tau_1 > \tau_2 > \tau_3 > \tau_4$.
I—the optimum temperature curve.

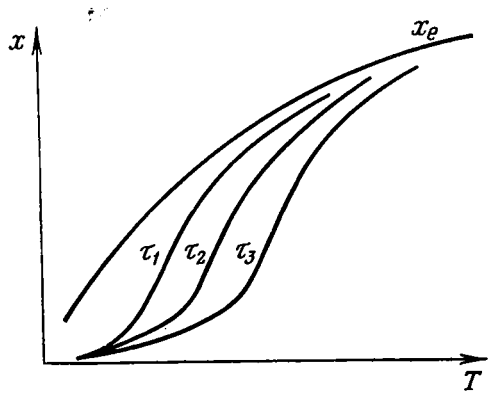


Fig. 4. The degree of conversion as a function of temperature in reversible endothermic reactions. $\tau_1 > \tau_2 > \tau_3$.

where E_1 and E_2 are the activation energies for the direct and reverse reactions. Hence

$$\frac{k_1}{k_2} = \frac{E_2}{E_1} \frac{[D]^{\nu'-\nu}}{[A]^{\alpha-\alpha'}[B]^{\beta-\beta'}} \tag{IV.31}$$

Introducing the equilibrium constant K through Eq. (IV.13) we obtain

$$K = \left(\frac{k_1}{k_2}\right)^{1/n} = \left(\frac{E_2}{E_1}\right)^{1/n} \frac{[D]^{\frac{\nu'-\nu}{n}}}{[A]^{\frac{\alpha-\alpha'}{n}}[B]^{\frac{\beta-\beta'}{n}}}$$

Using Eq. (IV.15) we obtain finally

$$K = \left(\frac{E_2}{E_1}\right)^{1/n} \frac{[D]^d}{[A]^a[B^b]} \tag{IV.32}$$

where K is the equilibrium constant at the optimum temperature and a, b, and d are the stoichiometric coefficients for the reaction.

If we know the temperature dependence of the equilibrium constant and the activation energy of the direct and reverse reactions as well as the reaction mechanism (the exponent n is determined by the reaction mechanism) we can calculate the optimum temperatures of a reversible exothermic reaction for any given reaction yield.

In practice the optimum temperatures are often calculated from the equilibrium temperatures found from the plot of equilibrium temperatures:

$$T_{opt} = \frac{T_e}{1 + \frac{2.3RT_e}{mQ_r} \log \frac{E + mQ_r}{E}} \tag{IV.33}$$

Here T_e is the equilibrium temperature (K), R is the gas constant (kJ/mole K), E is the activation energy (kJ/mole), m is the coefficient in the reaction equation for the component which is present in less than stoichiometric quantity, and Q_r is the heat of the reaction (kJ/mole).

Figure 4 shows that in endothermic reactions the equilibrium reaction yield increases with temperature. Therefore, such reactions should be conducted at the highest possible temperatures which are limited by the resistance of the reactor materials, the costs of maintaining high temperatures, decomposition of the reactants and reaction products, and other factors.

The economically optimal temperature for endothermic reactions is determined by comparing the costs of energy and heat-resistant materials with the economic benefits obtained by intensification of the process with increasing temperature.

Calculations of the Kinetic Parameters. Determination of the Optimum Temperatures

Problem 1. The rate of a chemical reaction at 450 °C is ten times that at 400 °C. Find the activation energy of the reaction if the driving force of the reaction does not change with temperature.

Solution. The reaction rate is given by Eq. (IV.1): $u = k\,\Delta C$. The reaction rate constant at 400 °C is k_1 and that at 450 °C is k_2. Eq. (IV. 27) yields

$$\frac{u_2}{u_1} = \frac{k_2}{k_1} = \frac{k_0 e^{-E/RT_2}}{k_0 e^{-E/RT_1}} = e^{E/R(1/T_1 - 1/T_2)}$$

Hence we obtain

$$\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\log e = \log 10; \quad \frac{E}{8.31}\left(\frac{1}{673} - \frac{1}{723}\right)\log e = 1$$

$$E = 174\,000 \text{ kJ/mole}$$

Problem 2 (see [2], p. 213). In catalytic decomposition of hydrogen peroxide with the initial concentration 25.4 mole/litre the solution contains 13.4 mole/litre H_2O_2 after 10 minutes, 7.08 mole/litre after 20 minutes, and 3.81 mole/litre after 30 minutes of reaction. Find the order of the reaction and calculate the reaction rate constant.

Solution. Let us assume that the reaction is of the first order. The reaction rate is given by Eq. (IV.22a):

$$\frac{dX_M}{d\tau} = k\,(a - X_M)$$

Hence we have

$$k = \frac{2.3}{\tau}\log\frac{a}{a - X_M}$$

Thus we can find the values of k at different moments:

$$k_1 = (2.3/10)\log(25.4/13.4) = 0.0634 \text{ min}^{-1}$$

$$k_2 = (2.3/20)\log(25.4/7.08) = 0.0638 \text{ min}^{-1}$$

$$k_3 = (2.3/30)\log(25.4/3.81) = 0.0633 \text{ min}^{-1}$$

It can be seen that k remains constant in the reaction. Hence, the reaction can be described by the first-order equation with the mean value of $k = 0.0635$ min^{-1}:

$$dX_M/d\tau = 0.0635\,(a - X_M)$$

Problem 3*. In 10 minutes 75.2% of benzene peroxide has been converted into diethyl ether at 60 °C (the first-order reaction). Find the reaction rate constant.

* Bartlet, P. D., Nozaki, K. *J. Am. Chem. Soc.*, 1947, vol. 69, p. 2999.

Solution. Eq. (IV.22) yields

$$k = (2.3/\tau) \log (a/(a - X_M)) = (2.3/10) \log (100/24.8) = 0.14 \text{ min}^{-1}$$

Problem 4 (see [1], p. 78) In the reaction between 0.5638 mole of sodium hydroxide and 0.3114 mole of acetic ether the amounts of reactants have been found to vary in the following way:

Time τ (s)	0	393	669	1010	1265
NaOH (moles)	0.5638	0.4866	0.4467	0.4113	0.3879
$CH_3COOC_2H_5$ (moles)	0.3114	0.2342	0.1943	0.1589	0.1354

Find the order of the reaction and the reaction rate constant.

Solution. The reaction is described by the equation

$$CH_3COOC_2H_5 + NaOH = C_2H_5OH + CH_3COONa$$

Assume that the reaction is irreversible and that the rate of formation of ethanol is proportional to the concentrations of sodium hydroxide and acetic ether (that is, the reaction is of the second order). The rate constant for a second-order reaction is

$$k = (2.3/\tau\ (a - b))\ \log\ (b\ (a - X)/a\ (b - X))$$

Hence, the rate constants at the specified moments are:

$$k_1 = (2.3/393\ (0.5638 - 0.3114)) \log (0.3114 \times 0.4866/0.5638 \times \times 0.2342) = 1.38 \times 10^{-3} \text{ s}^{-1} \text{ mole}^{-1}$$

$$k_2 = (2.3/669\ (0.5638 - 0.3114)) \log (0.3114 \times 0.4467/0.5638 \times \times 0.1943) = 1.42 \times 10^{-3} \text{ s}^{-1} \text{ mole}^{-1}$$

$$k_3 = (2.3/1010\ (0.5638 - 0.3114)) \log (0.3114 \times \times 0.4113/0.5638 \times 0.1589) = 1.40 \times 10^{-3} \text{ s}^{-1} \text{ mole}^{-1}$$

$$k_4 = (2.3/1265\ (0.5638 - 0.3114)) \log (0.3114 \times \times 0.3879/0.5638 \times 0.1354) = 1.43 \times 10^{-3} \text{ s}^{-1} \text{ mole}^{-1}$$

It can be seen that k is constant within the experimental accuracy so that the reaction is of the second order.

Problem 5. Find the activation energy for oxidation of sulphur dioxide to sulphur trioxide over the vanadium catalyst if the reaction rate constant is 6.3 s^{-1} at 455 °C, 12 s^{-1} at 470 °C and 26.2 s^{-1} at 490 °C.

Solution. *Method I.* The reaction rate constant as a function of temperature is given by Eq. (IV.27): $k = k_0 e^{-E/RT}$. This equation can be transformed into

$$\log k = \log k_0 - (E/RT) \log e$$

The experimental data can be used to plot log k as a function of $1/T$ (Fig. 5). The three experimental points are:

log k	0.8	1.08	1.418
$1/T$	1.37×10^{-3}	1.345×10^{-3}	1.31×10^{-3}

The slope of the plot in Fig. 5 yields the activation energy E:

$$\tan \alpha = E/R \log e = (1.3 - 0.8)/(1.32 - 1.37) \times 10^{-3} = 0.5/0.05 \times 10^{-3}$$

Hence, $E = 8.31 \times 10\,000/0.4343 = 192\,000$ kJ/mole.

Method II. Let us use Eq. (IV.30) and calculate the activation energy for various values of k and T:

$$E_1 = (19.1 T_1 T_2/(T_2 - T_1)) \log (k_2/k_1) = 193\,000 \text{ kJ/kmole}$$

$$E_2 = (19.1 T_1 T_3/(T_3 - T_1)) \log (k_3/k_1) = 188\,000 \text{ kJ/kmole}$$

$$E_3 = (19.1 T_2 T_3/(T_3 - T_2)) \log (k_3/k_2) = 184\,000 \text{ kJ/kmole}$$

The mean value of E is $(E_1 + E_2 + E_3)/3 = 188\,000$ kJ/kmole.

The method I yields directly the mean value of E.

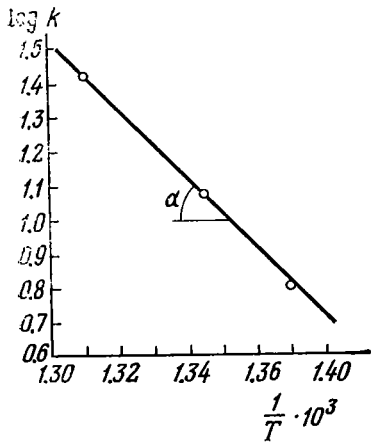


Fig. 5. Plot for calculating the activation energy (Problem 5).

Problem 6. Calculate the reaction rate constant for oxidation of sulphur dioxide over the iron oxide catalyst at 680 °C if the reaction rate is given by the simplified equation

$$dX/d\tau = k (X_e - X)/\sqrt{aX} \qquad \text{(IV.34)}$$

The concentration X_e at 680 °C is 0.58, the starting mixture contains 7% SO_2 and the rest is air. The experimental results for the reaction are:

τ (s)	0.06	0.1	0.19
X (relative units)	0.22	0.3	0.38

Solution. The experimental data can be used to plot X as a function of time τ (Fig. 6). The rate constant k can be found by graphical differentiation of this plot. According to Eq. (IV.34) we have $(dX/d\tau) = \sqrt{aX}/(X_e - X) = k$.

From the plot of Fig. 6 we have for $X_1 = 0.1$ and $\tau_1 = 0.02$ s tan $\alpha_1 = dX_1/d\tau_1 = (0.182 - 0.1)/(0.045 - 0.025) = 4.1$. Hence, $k_1 = 7.15$ s^{-1}. For $X_2 = 0.22$ and $\tau_2 = 0.06$ s tan $\alpha_2 = 2.1$,

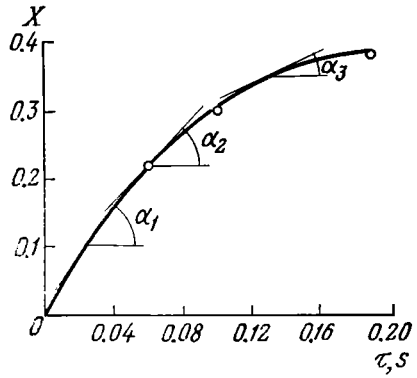


Fig. 6. Plot for calculating the reaction rate (Problem 6).

$k_2 = 7.25$ s^{-1}. For $X_3 = 0.35$ and $\tau_3 = 0.13$ s tan $\alpha_3 = 1.05$, $k_3 = 7.15$ s^{-1}. The mean value of k is $k = (k_1 + k_2 + k_3)/3 = 7.18$ s^{-1}.

Problem 7. Using the reaction rate constant for 680 °C (see Problem 6) find the reaction rate constant for 650 °C if the activation energy for the reaction is 184 000 kJ/kmole.

Solution. According to Eq. (IV.29) ln $(k_1/k_2) = (E/R)(1/T_2 - 1/T_1)$. Hence, 2.3 log $k_1 = 2.3$ log $7.18 + (184\,000/8.31\,(1/953 - 1/923)$ and $k_1 = 3.0$.

Problem 8. Find the order of the reaction between compounds A and B using the following data:

τ (min)	0	10	30.0
X (% of reacted components)	19.8	46.7	74.0

Solution. Assume that the reaction is of the first order for component A. Then the reaction rate constant is $k = (2.3/\tau)$ log $(a/(a - X))$. The values of k for 10 and 30 min of reaction are: $k_1 = (2.3/10)$ log $(0.802/(0.802 - 0.467)) = 0.088$ min^{-1}; $k_2 = (2.3/30)$ log $(0.802/(0.802 - 0.74)) = 0.086$ min^{-1}. Since k remains practically constant the reaction has the first order.

Problem 9. Find the reaction rate constant for synthesis of nitric oxide NO from the air at 2000 K. Experiments give the following

relationship between the content X of nitric oxide in the reaction mixture and the time τ of the reaction:

τ (s)	0.035	0.12	0.25	0.425	0.61
X (% by volume)	0.2	0.35	0.5	0.64	0.7

The rate constant k_r for the reverse reaction is given by the equation $\log k_r = -10.9 + 5.4 \times 10^{-3} T$.

Solution. The rate of the reaction $N_2 + O_2 \rightleftarrows 2NO$ is given by the equation similar to Eq. (IV.9):

$$u = dX/d\tau = k(a - 0.5X)(b - 0.5X) - k_r X^2$$

where a is the starting concentration of nitrogen (79% by volume), b is the starting concentration of oxygen (21% by volume), and

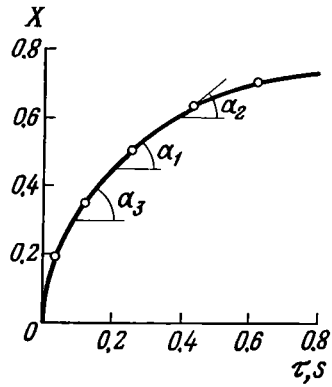


Fig. 7. Plot for calculating the reaction rate (Problem 9).

X is the concentration of NO in the reaction mixture at the moment τ (% by volume).

The rate constant for the reverse reaction at 2000 K is given by the equation

$$\log k_r = -10.9 + 0.0054 \times 2000 = -0.1$$

so that $k_r = 0.793\ s^{-1}$.

The values of $u = dX/d\tau$ can be found from the experimental plot of $X = f(\tau)$ (see Fig. 7). For $X_1 = 0.45$ we have $dX/d\tau = \tan \alpha_1 = 1$. Hence, $k_1 = (dX/d\tau + k_r X^2)/(a - 0.5X)(b - 0.5X) = (1 + 0.793 \times 0.45^2)/(79 - 0.5 \times 0.45)(21 - 0.5 \times 0.45) = 7.15 \times 10^{-4}\ s^{-1}$.

For $X_2 = 0.6$ we have $dX/d\tau = \tan \alpha_2 = 0.615$ and $k_2 = (0.615 + 0.793 \times 0.6^2)/(79 - 0.5 \times 0.6)(21 - 0.5 \times 0.6) = 5.53 \times 10^{-4}\ s^{-1}$.

For $X_3 = 0.3$ we have $dX/d\tau = \tan \alpha_3 = 1.425$ and $k_3 = (1.425 + 0.793 \times 0.3^2)/(79 - 0.5 \times 0.3)\ (21 - 0.5 \times 0.3) = 9.1 \times 10^{-4}\ s^{-1}$.

The above approximate values of k differ considerably owing to the small yields of the reaction and, hence, to low concentrations of nitric oxide in the reaction mixture. The mean value of k (taken for the three points) is $7.25 \times 10^{-4}\ s^{-1}$.

Problem 10. The starting gas mixture for synthesis of ammonia contains nitrogen and hydrogen. Find the ratio between the amounts of nitrogen and hydrogen which provides for the highest rate of the reaction $3H_2 + N_2 \rightleftarrows 2NH_3$.

Solution. Tre rate of ammonia synthesis can be described by the reaction equation derived by M. Temkin and V. Pyzhev:

$$u = k_1 p_{N_2} (p_{H_2}^3 / p_{NH_3}^2)^{0.5} - k_2 (p_{NH_3}^2 / p_{H_2}^3)^{0.5} \qquad \text{(IV.35)}$$

To find the maximum of this function we should find the ratio of reactants for which the first derivative of the function vanishes. To simplify the solution let us analyse two limiting cases: (1) the synthesis reactions occur far from the equilibrium; and (2) the reaction occurs near the equilibrium. In the first case we can ignore the reverse reaction and the effects of the reaction products on the rate of the direct reaction. Hence, we obtain

$$u = k p_{N_2} p_{H_2}^{1.5}$$

If x is the proportion of hydrogen in the reaction mixture then the proportion of nitrogen is $1 - x$ and the reaction rate is

$$u = k\,(1 - x)\,x^{1.5} = k\,(x^{1.5} - x^{2.5})$$

The first derivative is $u' = k \cdot 1.5\ x^{0.5} - k \cdot 2.5 x^{1.5} = 1.5\ kx^{0.5}\,(1 - 5x/3) = 0$. We find $1 - 5x/3 = 0$, $x = 3/5$, and $1 - x = 2/5$. Hence, $p_{H_2}/p_{N_2} = 3 : 2$, that is, the highest reaction rate in the first case is found for the hydrogen-nitrogen ratio of 3 : 2.

In the second case when reaction occurs near the equilibrium the rate of the reverse reaction cannot be ignored. Calculations similar to those made above show that in this case the highest reaction rate is given by the hydrogen-nitrogen ratio of 3 : 1.

Problem 11. Calculate the optimal temperature profile of the column for methanol synthesis from carbon monoxide and hydrogen. Methanol yield increases from 1 to 5%. The reaction is carried out at 3.03×10^7 Pa (300 at) with stoichiometric ratio of H_2 and CO according to the equation $CO + 2H_2 \rightleftarrows CH_3OH$. The activation energies for the direct and reverse reactions are $E_1 = 109\,000$ kJ/kmole and $E_2 = 155\,000$ kJ/kmole, respectively. The limiting stage of methanol synthesis is hydrogen adsorption at the

surface of the solid catalyst (see below, Chapter VI). The content of the inert gases in the reaction mixture is 13%.

Solution. (see Chapter II, Problem 12). If the limiting stage of methanol synthesis is hydrogen adsorption the reaction rate can be described by the following equation:

$$u = k_1 p_{H_2} \frac{p_{CO}^{0.25}}{p_{CH_3OH}^{0.25}} - k_2 \frac{p_{CH_3OH}^{0.25}}{p_{CO}^{0.25}} \qquad \text{(IV.36)}$$

where k_1 is the rate constant of the direct reaction, k_2 is the rate constant of the reverse reaction, and p_{H_2}, p_{CO}, p_{CH_3OH} are the partial pressures of hydrogen, carbon monoxide and methanol, respectively.

To find the optimum temperature we can use the equilibrium constant at the optimum temperature according to Eq. (IV.32):

$$K_p = (E_2/E_1)^{1/n} (p_{CH_3OH}/p_{H_2}^2 p_{CO})$$

The parameter n can be found from Eq. (IV.15): $n = (1 - 0)/2 = (0.25 - (-0.25))/1 = (0.25 - (-0.25))/1 = 1/2$. Hence, $K_p = (E_2/E_1)^2 (p_{CH_3OH}/p_{H_2}^2 p_{CO})$.

Let us calculate the equilibrium constant and the respective optimum temperature for various methanol yields (1%, 2%, 3%, 4%, and 5%).

For the methanol yield of 1% we have $p_n = 3 \times 10^7 \times 0.13 = 0.39 \times 10^7$ Pa (neutral gases); $p_{CH_3OH} = 3 \times 10^7 \times 0.01 = 3 \times 10^5$ Pa; $p_{CO+H_2} = 3 \times 10^7 - 0.39 \times 10^7 - 0.03 \times 10^7 = 2.58 \times 10^7$ Pa; $p_{CO} = 2.58 \times 10^7/3 = 0.86 \times 10^7$ Pa; $p_{H_2} = 2 \times 2.58 \times 10^7/3 = 1.72 \times 10^7$ Pa; $K_p^{I} = (155\,000/109\,000)^2 \times (0.03 \times 10^7/(1.72 \times 10^7)^2 \times 0.86 \times 10^7 = 2.39 \times 10^{-16}$ Pa^{-2} $= 2.39 \times 10^{-6}$ at^{-2}.

For the methanol yield of 2% we have $p_{CH_3OH} = 3 \times 10^7 \times 0.02 = 0.06 \times 10^7$ Pa; $p_{CO+H_2} = 2.55 \times 10^7$ Pa; $p_{CO} = 0.85 \times 10^7$ Pa; $p_{H_2} = 1.7 \times 10^7$ Pa; $K_p^{II} = 4.95 \times 10^{-16}$ Pa^{-2} $= 4.95 \times 10^{-6}$ at^{-2}.

For the methanol yield of 3% we have $p_{CH_3OH} = 0.09 \times 10^7$ Pa; $p_{CO+H_2} = 2.52 \times 10^7$ Pa; $p_{CO} = 0.84 \times 10^7$ Pa; $p_{H_2} = 1.68 \times 10^7$ Pa; $K_p^{III} = 7.66 \times 10^{-16}$ Pa^{-2} $= 7.66 \times 10^{-6}$ at^{-2}.

For the methanol yield of 4% we have $p_{CH_3OH} = 0.12 \times 10^7$ Pa; $p_{CO} = 0.83 \times 10^7$ Pa; $p_{H_2} = 1.66 \times 10^7$ Pa; $K_p^{IV} = 10.6 \times 10^{-16}$ Pa^{-2} $= 10.6 \times 10^{-6}$ at^{-2}.

For the methanol yield of 5% we have $p_{CH_3OH} = 0.15 \times 10^7$ Pa; $p_{CO+H_2} = 2.46 \times 10^7$ Pa; $p_{CO} = 0.82 \times 10^7$ Pa; $p_{H_2} = 1.64 \times 10^7$ Pa; $K_p^{V} = 13.75 \times 10^{-16}$ Pa^{-2} $= 13.75 \times 10^{-6}$ at^{-2}.

The following empirical relationship has been found between optimum temperature and equilibrium constant for methanol synthesis in the temperature range from 300 to 400 °C and under the pressure

3.0×10^7 Pa (300 at):

$$\frac{|\log K_p|}{13} + \frac{10^3/T_{opt}}{27.6} = 1 \qquad \text{(IV.37)}$$

Here K_p is given in at^{-2} units.

Substituting the above equilibrium constant values in Eq. (IV.37) we can find the optimum temperatures. We obtain $T^{I}_{opt} = 639$ K =

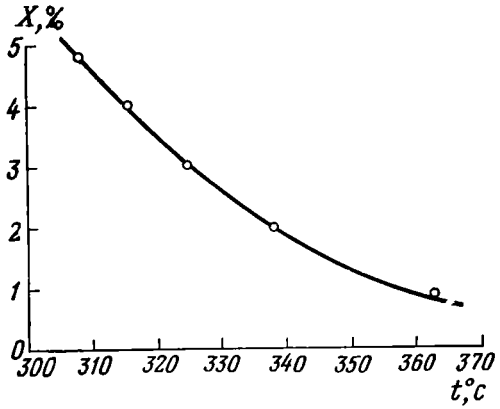


Fig. 8. The optimum temperature plot (Problem 11).

= 366 °C; $T^{II}_{opt} = 611$ K = 338 °C; $T^{III}_{opt} = 597$ K = 324 °C; $T^{IV}_{opt} =$ = 588 K = 315 °C; and $T^{V}_{opt} = 580$ K = 307 °C.

The results can be used to plot the curve of optimum temperatures (Fig. 8)

Further Problems for Students

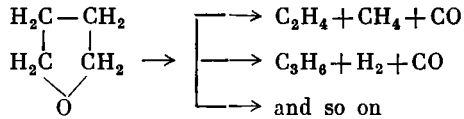
1. Find the activation energy of a reaction if the reaction rate at 500 °C is 7 times that at 430 °C.
2. Find the activation energy and the reaction rate constant for decomposition of a compound A in an aqueous solution. At 10 °C the rate constant is 1.1×10^{-4} s^{-1} and it is 5.5×10^{-2} s^{-1} at 60 °C.
3. A gas mixture contains nitric oxide and air. Find the oxygen concentration which provides for the maximum rate of oxidation of nitric oxide. The temperature of the gas mixture is below 150 °C, that is, the process is practically irreversible. Make use of the equation $u = k\,[NO]^2[O_2]$.
4. Find variation of the rate of the reaction $2NO + O_2 \rightarrow 2NO_2$ with the two-fold increase of the initial oxygen concentration and with the two-fold increase of the initial concentration of NO.

5. A polimerization reaction occurs at a constant temperature in homogeneous phase. For the initial monomer concentration of 0.3, 0.5, and 0.9 mole/litre 30% of the monomer reacts in 40 minutes. Find the reaction rate.

6. The rate of the reaction $2A + B \rightarrow D$ is given by the first-order equation for each component. After 20 minutes 20% of the component A has reacted. What is the concentration of the component A in 40 minutes?

7. For the consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ find the time when the concentration of B reaches the maximum if $k_1 = 2k_2$.

8 (see [5]). Find the overall equation for the rate of thermal decomposition of tetrahydrofuran:



The half-lives of the reaction:

τ (min)	14.5	67	11.7	57	45
p_0 (Pa)	27 060	27 193	37 324	17 330	27 460
T (°C)	569	530	560	550	539

9. Find the H_2: CO ratio providing for the highest rate of methanol synthesis if the reaction rate is given by the equation

$$u = k_1 p_{H_2} \frac{p_{CO}^{0.25}}{p_{CH_3OH}^{0.25}} - k_2 \frac{p_{CH_3OH}^{0.5}}{p_{CO}^{0.25}}$$

Chapter V

Primary Mathematical Models of Reactors

Introduction

Chemical reactor is an apparatus for carrying out chemical technological processes which comprise chemical reactions and the mass- and heat-transfer processes. The type and quality of reactor largely determine the efficiency of the process.

The industrial reactors should satisfy the following basic requirements:

(1) the highest productivity and intensity of operation;
(2) high product yields;
(3) low energy consumption, the best utilization of the reaction heat;
(4) simplicity of design and low construction cost;
(5) easy control.

It is not always that all these requirements can be met. The ultimate choice is determined by the costs-benefits analysis.

Numerous types of reactors are used to carry out different chemical processes. Classification of the reactor types can be done according to different characteristics. The most convenient for calculations is the classification of reactors by the time of operation, namely, (1) batch-process reactors and (2) continuous-process reactors with the steady or non-steady flows.

This classification of reactors is applicable both to the homogeneous processes and to heterogeneous processes occurring in the kinetic region since their mathematical descriptions are similar.

The modern large-scale chemical industries make use mostly of the continuous-process reactors which, typically, require numerous auxiliary units but make possible reliable control of the product quality. The batch-process reactors are more efficient in small-scale production.

The design and capacity of a reactor are determined by (1) the rates of the chemical reaction and the heat- and mass-transfer processes and (2) the hydrodynamic parameters.

Mathematical analysis of a process is always based on the material balance of the process drawn up for one of the components of the reaction mixture. According to the law of conservation of mass the mass of the materials fed to the system is equal to the mass of the products discharged from the system and the mass of the materials left in the system.

The material balance can be written as differential equations for the elementary volume. The material balance equation for the main component contains the following terms:

$$\begin{pmatrix}\text{The amount } G_f \text{ of the component}\\ \text{fed the elementary volume per}\\ \text{unit time}\end{pmatrix}=\begin{pmatrix}\text{The amount } G_d \text{ of the component}\\ \text{discharged from the elementary}\\ \text{volume per unit time}\end{pmatrix}+$$

$$+\begin{pmatrix}\text{The rate } G_r \text{ of consumption of}\\ \text{the component in the chemical}\\ \text{reaction in the elementary volume}\end{pmatrix}+\begin{pmatrix}\text{The rate } G_a \text{ of accumu-}\\ \text{lation of the component}\\ \text{in the elementary volume}\end{pmatrix} \quad (V.1)$$

If the concentration of the component is uniform over the volume of the reactor the material balance equation can be written for the whole reactor. If the concentration varies over the reaction zone the material balance equation is drawn up for the elementary volume and then the equation is integrated according to the distribution of flows and concentrations in the reaction zone.

If the process occurs under non-isothermic conditions the material balance should be complemented by the heat balance. Like the material balance, the heat balance can be written in the following form:

$$\begin{pmatrix}\text{The heat fed to the}\\ \text{elementary volume}\\ \text{per unit time}\end{pmatrix}=\begin{pmatrix}\text{The heat removed from}\\ \text{the elementary volume}\\ \text{per unit time}\end{pmatrix}+$$

$$+\begin{pmatrix}\text{The rate of heat consumption}\\ \text{in the elementary volume owing}\\ \text{to the chemical reaction}\end{pmatrix}+\begin{pmatrix}\text{The rate of accumulation}\\ \text{of heat in the elementary}\\ \text{volume}\end{pmatrix} \quad (V.2)$$

The following three types of idealized reactor models are typically used in calculations:

(1) batch reactor with complete mixing;
(2) flow-through ideal plug-flow reactor;
(3) flow-through reactor with complete mixing.

Batch reactor with complete mixing. The apparatus is filled with the starting materials which remain there for a certain time until a required yield of products is obtained. Then the mixture of products is discharged from the reactor. In the reactor of this type the composition of the reaction mixture is uniform over the volume and continuously varies with time.

The material balance for the batch-process reactor can be derived from Eq. (V.1) where $G_f = 0$ and $G_d = 0$:

$$u_A v + dG/d\tau = 0 \quad (V.3)$$

Here v is the volume of the reaction zone.
We have

$$dG/d\tau = d(G_1(1 - x_A))/d\tau = -G_1 \frac{dx_A}{d\tau} \quad (V.4)$$

where G_1 is the initial amount of the starting material and x_A is the degree of conversion of the starting material. Substitution of Eq. (V.5) in Eq. (V.3) yields

$$u_A v = G_1 \frac{dx_A}{d\tau} \tag{V.5}$$

Integration of Eq. (V.5) yields

$$\tau = G_1 \int_0^{x_A} dx_A / u_A v \tag{V.6}$$

Eq. (V.6) gives the time needed for obtaining the required yield of products in a batch-process reactor. If the reaction volume is constant Eq. (V.6) can be written as

$$\tau = \frac{G_1}{v} \int_0^{x_A} \frac{dx_A}{u_A} = C_1 \int_{C_1}^{C_f} \frac{dx_A}{u_A} \tag{V.7}$$

where C_1 is the initial concentration of the starting material.

If the reaction volume v varies Eq. (V.6) can be transformed into

$$\tau = G_1 \int_0^{x_A} \frac{dx_A}{u_A v_1 (1+\beta x_A)} = C_1 \int_0^{x_A} \frac{dx_A}{u_A (1+\beta x_A)} \tag{V.8}$$

where $\beta = \frac{v_{x_A=1} - v_{x_A=0}}{v_{x_A=0}}$

Equations (V.6)-(V.8) can be used to determine the capacity of the isothermic batch-process reactor. To apply these equations to non-isothermic processes we should know the temperature dependence of the reaction rate and the relationship between the reaction yield and the heat liberated in the reaction.

The ideal plug-flow reactor. In the reactor of this type any volume element of the reaction mixture travels along the reactor parallel to other elements without any mixing between them.

Figure 9 illustrates variation of the degree of conversion x, starting concentrations C, and other parameters in the ideal plug-flow reactor. If there is no accumulation of material in the reactor ($G_a = 0$) the material balance can be written as

$$G_f = G_d + G_r \tag{V.9}$$

or

$$G_f = C_A V_m (1 - x_A) \tag{V.10}$$

where V_m is the volumetric flow rate of the reaction mixture,

$$G_d = C_A V_m (1 - x_A - dx_A) \tag{V.11}$$

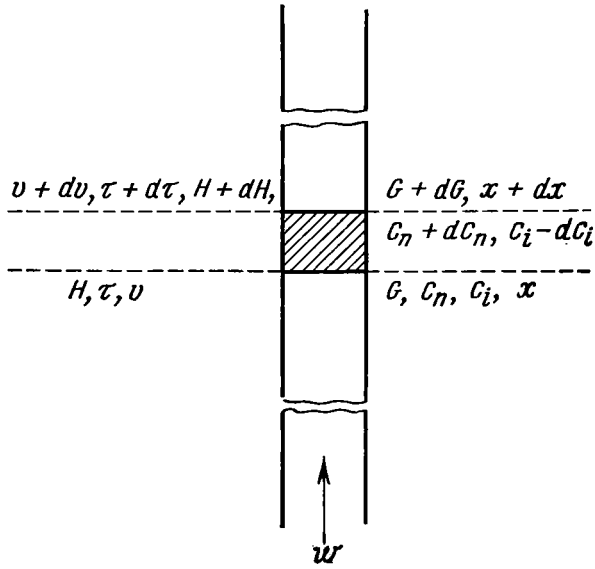


Fig. 9. Schematic diagram of the ideal plug-flow reactor.

and

$$G_r = u_A dv \tag{V.12}$$

Substitution of Eqs. (V.10)-(V.12) in Eq. (V.9) yields

$$V_m C_A dx_A = u_A dv \tag{V.13}$$

and

$$\tau = v/V_m = C_1 \int_{x_1}^{x_f} dx_A/u_A \tag{V.14}$$

For the nth-order reaction without variation of volume we obtain

$$\tau = C_{A_1} \int_0^x \frac{dx_A}{kC_A^n} = C_{A_1} \int_0^x \frac{dx_A}{kC_{A_1}^n (1-x_A)^n} = \frac{1}{kC_{A_1}^{n-1}} \int_0^x \frac{dx_A}{(1-x_A)^n} \tag{V.15}$$

For $n = 0$ we have

$$\tau = C_{A_1} x_A / k \tag{V.16}$$

and for $n = 1$

$$\tau = \frac{1}{k} \ln \frac{1}{1-x_A} \tag{V.17}$$

If the volume varies with the reaction we obtain

$$\tau = \frac{1}{kC_{A_1}^{n-1}} \int_0^x \frac{(1+\beta x_A)^n \, dx_A}{(1-x_A)^n} \qquad (V.18)$$

For the irreversible reaction of the first order we have

$$\tau = \frac{1}{k}\left[(1+\beta)\ln\frac{1}{1-x_A} - \beta x_A\right] \qquad (V.19)$$

For the irreversible reaction of the second order we have

$$\tau = \frac{1}{kC_{A_1}}\left[2\beta(1+\beta)\ln(1-x_A) + \beta^2 x_A + (\beta+1)^2 \frac{x_A}{1-x_A}\right] \qquad (V.20)$$

For the reversible reaction of the type

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B$$

in which the direct and reverse reactions can be described by the first-order kinetic equations we can write the following equation for the ideal plug-flow reactor:

$$\tau = \frac{1}{k_1}\left[\frac{\beta x_A}{L} - \frac{L+\beta}{L^2}\ln(1-Lx_A)\right] \qquad (V.21)$$

Here $L = 1 + (k_2/k_1)(1 + \beta)$.

If the rate of reaction is given by an equation of a higher or fractional order the respective equations are so bulky that they can be solved only by computer or graphical techniques.

The reactor with complete mixing. In the reactor of this type any volume element of the reaction mixture is instantaneously mixed with the entire volume of the reaction mixture since the velocities of circulation flows along and across the reactor are much higher than that of the flow through reactor.

The degree of mixing is evaluated with the diffusion criterion Pe′:

$$\mathrm{Pe}' = wH/D_e \qquad (V.22)$$

Here w is the linear velocity of the gas or liquid in the reactor (m/s), H is the height of the reaction zone, and D_e is the effective diffusion coefficient (m^2/s).

The flows in the reactor with complete mixing are illustrated in Fig. 10. In such reactors the concentration of any component is uniform over the entire volume of the reactor so that the material balance equation can be written for the whole reactor. For the steady-state operation we have

$$G_f = G_d + G_r \qquad (V.23)$$

and

$$V_m C_1 = V_m C_1 (1 - x_f) + u_{A_f} v \qquad (V.24)$$

where x_f is the final degree of conversion. Eq. (V.24) yields

$$V_m C_1 x_f = u_{A_f} v \tag{V.25}$$

and

$$v/V_m = C_1 x_f / u_{A_f} = \tau \tag{V.26}$$

Since $x_f = (C_1 - C_f)/C_1$ we have

$$\tau = (C_1 - C_f)/u_{A_f} \tag{V.27}$$

Equations (V.26) and (V.27) are the characteristic equations for the flow-through reactor with ideal mixing which can be used to cal-

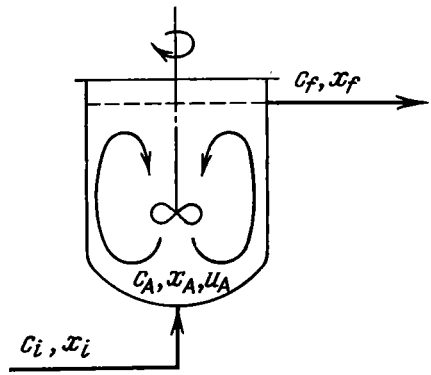


Fig. 10. Schematic diagram of the reactor with complete mixing.

culate unknown parameters from the given ones. The reactor capacity, consumption of reactants, and the initial and final concentrations can be determined only if the kinetics of the process is known.

Cascade of reactors with complete mixing. In a cascade of reactors the composition of the reaction mixture varies from one reactor to another. At each stage of the cascade the process parameters are uniform over the reactor volume (see Fig. 11).

Let us draw up the material balance for the cascade of n reactors with complete mixing assuming a first-order reaction without variation of volume ($\beta = 0$). We obtain for the jth reactor

$$\tau_j = \frac{v_j}{V_m} = \frac{C_1 v_j}{G_1} = \frac{C_1 (x_j - x_{j-1})}{u_j} \tag{V.28}$$

$$\tau_j = \frac{C_1 \left[\left(1 - \frac{C_j}{C_1}\right) - \left(1 - \frac{C_{j-1}}{C_1}\right) \right]}{u_j} = \frac{C_{j-1} - C_j}{kC_j} \tag{V.29}$$

so that $C_{j-1}/C_j = 1 + k\tau_j$

The time τ should be the same for all n reactors whose volumes v_j are identical so that we obtain

$$\frac{C_1}{C_f} = \frac{C_1}{C_1} \cdot \frac{C_1}{C_2} \cdot \frac{C_2}{C_3} \cdots \frac{C_{n-1}}{C_f} = (1 + k\tau_j)^n \qquad \text{(V.30)}$$

For the whole cascade of reactors we obtain

$$\tau = n\tau_j = \frac{n}{k}\left[\left(\frac{C_1}{C_f}\right)^{1/n} - 1\right] \qquad \text{(V.31)}$$

Eq. (V.31) can be used to determine the capacity of the cascade, the number of reactors in the cascade or the product yield from the known other parameters.

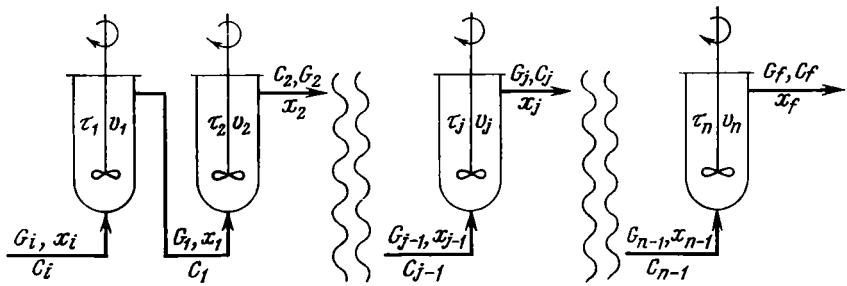


Fig. 11. Cascade of reactors with complete mixing.

For the second-order reaction in the cascade of n reactors we can write equations which are similar to those for the first-order reaction occurring under the same conditions:

$$C_f = \frac{1}{2k\tau_j}\left(-1 + \sqrt{-1 \ldots + 2\sqrt{-1 + 2\sqrt{1 + 4C_1 k\tau_j}^{n=1}}}^{n}\right). \qquad \text{(V.32)}$$

Eqs. (V.31) and (V.32) show that when the number n of reactors in the cascade is increased to provide for a given product yield the volume of the system decreases to the volume of the ideal plug-flow reactor which provides for the same product yield at a constant temperature in the kinetic region. However, this is the idealized picture since the ideal plug-flow reactor cannot be isothermic even in the kinetic region. In fact, the process in the plug-flow reactors occurs in the diffusion region at the temperatures far from the optimum. Therefore the process rates in the plug-flow reactors are lower than in the reactor cascades and, hence, the reaction volume is larger. This is why the reactor cascades are used. Equations of the type of Eqs. (V.31) and (V.32) yield the number and capacities of the reactors for a known kinetics of a process.

In calculations for reactors graphical techniques are widely used. Let us discuss the graphical technique for calculating the parameters of a cascade of the reactors with complete mixing suggested by Jones*.

Let us transform Eq. (V.29) into

$$u_j = -C_j/\tau_j + C_{j-1}/\tau_j \qquad \text{(V.33)}$$

For a given input concentration C_{j-1} this equation gives a linear relationship between the output concentration and the reaction rate. The straight line representing this relationship intersects the

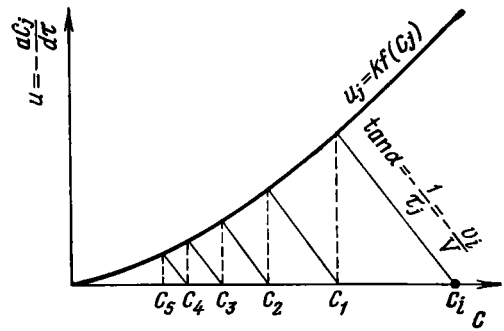


Fig. 12. Plot for calculating the parameters of a cascade of complete-mixing reactors (durations of residence of reactants in all reactors are identical).

abscissa axis at the point C_{j-1} and has the slope $1/\tau_j$. Moreover, the values of u_j and C_j should satisfy the equation $u_j = kC_j$ (or $u = kf(C_j)$ in the general form) for the reaction rate. Thus, the plot for Eq. (V.33) intersects the reaction rate *vs.* concentration plot at the point corresponding to C_j (see Fig. 12). When C_j has been found calculations are repeated to find C_{j+1} for the next reactor of the cascade. If the times of residence of reactants in the reactors are identical (the reactors of the cascade have identical capacities) the plots given by Eq. (V.33) are parallel. If the number of reactors and the final product yield are given the time of residence in the reactor is selected by trial and error. This can be done only if the reaction rate can be expressed as a function of one variable ($u_j = kf(C_j)$).

Calculations of Reactors of Various Types

Problem 1. The reversible exothermic process of oxidation of SO_2 in a single bed of vanadium catalyst is carried out in an ideal plug-flow reactor. The reaction is described by the following equa-

* Jones R. W. *Chem. Eng. Progr.*, 1951, vol. 47, p. 46.

tion:

$$SO_2 + 0.5O_2 \rightleftarrows SO_3$$

The temperature of the catalyst bed is 570 °C and is assumed to be constant over the bed. The starting gas has the following composition (in % by volume): SO_2—11, O_2—10, and N_2—79. The consumption of gas is 15 500 m³/h. The velocity of the gas flow in the reactor is $w = 1.4$ m/s. The reaction rate constant at 585 °C is 13.7. The equilibrium constant is given by

$$\log K_p = 4905/T - 4.6455 \qquad \text{(V.34)}$$

The activation energy is $E = 87\,800$ kJ/mole. The reserve factor is $c = 1.3$.

Calculate the reaction volume of the reactor, that is the volume of the catalyst bed, which would provide for the degree of conversion of 0.5, and the diameter of the reactor and the height of the catalyst bed.

Solution. Equation (V.14) for the ideal plug-flow reactor yields

$$\tau = v/V_m = C_1 \int_0^x dx/u$$

The rate of the oxidation reaction in the vanadium catalyst bed is given by the approximate equation derived by G. Boreskov:

$$u = \frac{k}{2a}\left(\frac{x_e - x}{x}\right)^{0.8}(2b - ax)\frac{273}{T} \qquad \text{(V.35)}$$

Here a is the initial content of SO_2 in the reaction mixture (% by volume), b is the initial content of O_2 (% by volume) and x_e is the equilibrium degree of conversion.

Substitution of Eq. (V.35) into Eq. (V.14) yields

$$\tau = \frac{v}{V_m} = \int_0^x \frac{dx}{\frac{k}{2a}\left(\frac{x_e - x}{x}\right)^{0.8}(2b - ax)\frac{273}{T}} \qquad \text{(V.36)}$$

To integrate Eq. (V.36) we can plot $1/u$ as a function of x and find the area corresponding to $0 \leqslant x \leqslant 0.5$.

First we should find the reaction rate constant at 570 °C from that at 585 °C using Eq. (IV.29): $2.3 \log (13.7/k) = 87\,800/8.31)(1/843 - 1/858) = 0.222$, $\log k = 1.04$, $k = 11.0$.

The equilibrium degree of conversion can be determined as the ratio of equilibrium concentrations:

$$x_e = G_e/G_{max} = C_{e_{SO_2}}/(C_{e_{SO_2}} + C_{e_{SO_3}})$$

Another equation using the equilibrium constant and the starting concentrations is

$$x_e = \frac{K_p}{K_p + \sqrt{\frac{100 - 0.5ax_e}{b - 0.5ax_e}}} \qquad (V.37)$$

At 570 °C we have $\log K_p = 4905/843 - 4.645 = 1.18$ and $K_p = 15.15$. Hence, we have

$$x_e = \frac{15.15}{15.15 + \sqrt{\frac{100 - 0.5 \times 11x_e}{10 - 0.5 \times 11x_e}}} \qquad (V.38)$$

Eq. (V.38) yields $x_e = 0.79$.

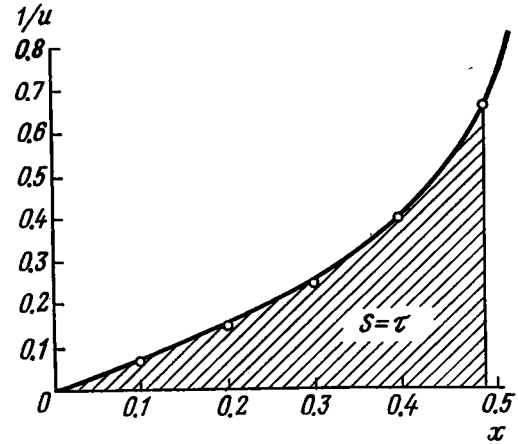


Fig. 13. Plot for calculating the reaction time (Problem 1).

We can now calculate the values of $1/u$ for several arbitrary values of x using Eq. (V.35):

$$1/u = \frac{2a}{k}\left(\frac{x}{x_e - x}\right)^{0.8}\left(\frac{1}{2b - ax}\right)\frac{843}{273}$$

$$1/u_1 = 0.069, \quad x_1 = 0.1$$
$$1/u_2 = 0.145, \quad x_2 = 0.2$$
$$1/u_3 = 0.248, \quad x_3 = 0.3$$
$$1/u_4 = 0.4, \quad x_4 = 0.4$$
$$1/u_5 = 0.655, \quad x_5 = 0.5$$

Using these points we can plot $1/u$ vs. x (Fig. 13). Graphical integration yields $\tau = 0.117$ s ≈ 0.12 s. The volume of the catalyst (the reaction volume) is $V = 0.12 \times 15\,500 \times 1.3/3600 = 0.675$ m³. The cross section of the reactor is $S = V_m/w = 15\,500 \times 843/3600 \times 273 \times 1.4 = 9.5$ m². The diameter of

the reactor is $D = \sqrt{4S/\pi} = 3.48$ m. The height of the catalyst layer is $v/S = 0.071$ m.

Problem 2 (see [17]). The gas discharged from the reactor for ammonia oxidation is rapidly cooled for condensation of steam in it. The gas contains 82 mol. % of nitrogen, 9 mol. % of nitric oxide, 1 mol. % of nitrogen dioxide and 8 mol. % of oxygen. Then the gas is oxidized to obtain the $NO_2 : NO$ ratio of 5 : 1 and is fed to absorption columns to produce nitric acid. Cooling is assumed to be sufficiently effective to maintain the constant temperature of 20 °C. The consumption of gas fed to the reactor is 10 000 m^3/h and the gas pressure is 10^5 Pa.

Calculate the volume of the plug-flow reactor for carrying out the process.

Solution. The reaction $2NO + O_2 = 2NO_2$ is a homogeneous gas reaction which is practically irreversible. Assume that the reaction rate is proportional to $[NO]^2[O_2]$. If the concentrations are expressed in moles per litre and time in seconds the reaction rate constant at 20 °C is 1.4×10^4 $litre^3/mole^2$ s.

The reaction time and the reaction volume for the ideal plug-flow reactor are given by Eq. (V.14):

$$\tau = v/V_m = C_1 \int_{x_1}^{x_f} dx/u; \quad v = G_1 \int_{x_1}^{x_f} dx/u$$

The reaction rate is $u = kC_{NO}^2 C_{O_2}$ where C_{NO} and C_{O_2} are the instantaneous concentrations of the reactants. Let us express these concentrations in terms of the initial concentrations and the numbers of the reacted moles. One mole of the starting mixture contains 0.09 mole NO, 0.01 mole NO_2, 0.08 mole O_2, and 0.82 mole N_2. By the moment τ x moles of NO and $0.5x$ moles of O_2 have reacted and x moles of NO_2 have been formed. The product mixture contains (per 1 mole of the starting mixture)$(0.09 - x)$ mole of NO, $(0.01 + x)$ mole of NO_2, $(0.08 - 0.5x)$ mole of O_2 and 0.82 mole of N_2. The total is $(1 - 0.5x)$ mole.

The volume of $(1 - 0.5x)$ mole of the reaction mixture at the temperature T and the pressure P is

$$V = (1 - 0.5x)\ 22.4T \times 1/P \times 273$$

The concentrations of reactants (in moles per litre) by the moment τ are

$$C_{NO} = \frac{0.09 - x}{(1 - 0.5x)\frac{22.4T \cdot 1}{P \cdot 273}}$$

$$C_{O_2} = \frac{0.08 - 0.5x}{(1 - 0.5x)\frac{22.4T \cdot 1}{P \cdot 273}}$$

Substitution of these concentrations in Eq. (V.14) yields

$$v = G_1 \int_{x_1}^{x_f} \frac{dx}{k\left[\dfrac{0.09-x}{(1-0.5x)\dfrac{22.4T\cdot 1}{P\cdot 273}}\right]^2 \left[\dfrac{0.08-0.5x}{(1-0.5x)\dfrac{22.4T\cdot 1}{P\cdot 273}}\right]} \qquad \text{(V.39)}$$

which can be transformed into

$$v = \frac{G_1}{k} \int_{x_1}^{x_f} \frac{(0.082)^3 T^3 (1-0.5x)^3 \, dx}{P^3 (0.09-x)^2 (0.08-0.5x)} \qquad \text{(V.40)}$$

Let us find the limits of integration in Eq. (V.40). By the moment τ the reaction mixture contains $(0.01 + x)$ mole of NO_2 and $(0.09 - x)$ mole of NO. The required NO_2 : NO ratio is 5 : 1, that is, $(0.01 + x)/(0.09 - x) = 5/1$ and we obtain $x = 0.0733$.

Thus, Eq. (V.40) can be written as

$$v = \frac{G_1}{k} \int_{0}^{0.0733} \frac{(0.082)^3 T^3 (1-0.5x)^3 \, dx}{P^3 (0.09-x)^2 (0.08-0.5x)} \qquad \text{(V.41)}$$

The mass flow rate is $G_1 = 10\,000$ m³/h $= 10^4/3.6$ litre/s $= 10^4/3.6 \times 22.4$ mole/s. Substituting the numerical values in Eq. (V.41) we obtain

$$v = \frac{10^4 (0.083)^3 293^3}{3.6 \times 22.4 \times 1.4 \times 10^4} \int_{0}^{0.0733} \frac{(1-0.5x)^3 \, dx}{(0.09-x)^2 (0.08-0.5x)} \qquad \text{(V.42)}$$

Eq. (V.42) can be integrated by plotting (see Fig. 14) the integrand y as a function of x through a few calculated points ($x = 0$, $y = 1545$; $x = 0.02$, $y = 2830$; $x = 0.04$, $y = 6270$; $x = 0.06$, $y = 20\,200$; $x = 0.07$, $y = 50\,000$). The area under the plot is 950. Hence, we obtain $v = 1.1 \times 10^5$ litre $= 110$ m³.

Problem 3. Hydrolysis of acetic anhydride is carried out in a complete-mixing reactor with an agitator. The concentration of acetic anhydride in the starting mixture is $C_1 = 0.3$ mole/litre. The degree of conversion (with respect to the starting mixture) is $x_f = 0.7$. The flow rate of the starting mixture is constant: $V_m = 20$ litres/min. A large excess of water is used. The reaction rate constant is $k = 0.38$ min^{-1}.

Find (1) the volume of a single complete-mixing reactor providing for the specified degree of conversion, (2) the reaction volume of the ideal plug-flow reactor for the same process, and (3) the number of stages of a cascade of complete-mixing reactors whose total volume is close to that of the plug-flow reactor.

Solution. The rate of hydrolysis of acetic anhydride with a large excess of water can be expressed by a first-order equation $u = kC$.

(1) Eq. (V.26) yields the volume of the complete-mixing reactor: $v = V_m C_1 x_f / u$, where $u = kC_f$. The final concentration of acetic

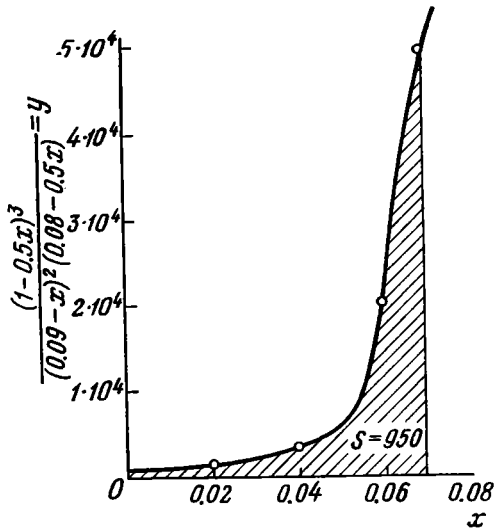


Fig. 14. Plot for calculating the reaction time (Problem 2).

anhydride is $C_f = C_1 (1 - x_f) = 0.3 (1 - 0.7) = 0.09$ mole/litre. Hence we find $v = 123$ litres.

(2) Eq. (V.14) can be used to find the volume of the isothermic ideal plug-flow reactor for the process assumed to occur in the kinetic region:

$$v = V_m \int_{C_1}^{C_f} dC/u = V_m \int_{C_1}^{C_f} \frac{dC}{-kC} = \frac{V_m \cdot 2.3}{k} \log \left(\frac{C_1}{C_f} \right) = 63.5 \text{ litres}$$

(3) The total time of residence of the reactants in a cascade of reactors is given by Eq. (V.31):

$$\tau = v/V_m = \frac{n}{k} \left[\left(\frac{C_1}{C_f} \right)^{1/n} - 1 \right]$$

We find for $n = 1$, 2, 3, 4, 6 and ∞ the following total volumes: $v = 123$, 86.5, 77.8, 73.8, 69.5, 63.5 litres, respectively. It can be seen that after $n = 3$ the decrease of the total volume with n becomes slow. Thus, three stages in the cascade are sufficient since the reactors with stirrers are expensive and a plant with a larger number of stages becomes too large.

Problem 4. The reaction $2A \rightleftarrows B + C$ is carried out continuously in a cascade of three reactors with agitators. The flow rate of reac-

tants is $V = 10$ m³/h. The starting solution contains 1.5 kmole/m³ of the component A and no components B and C. The rate constant of the direct reaction is $k_1 = 10$ m³/kmole h and the equilibrium constant is $K_p = 16.0$. The degree of conversion should be 80% of the equilibrium one.

Find the volume of one reactor of the cascade assuming that the reactor volumes are identical.

Solution. The equilibrium concentration of the component A can be found from the equilibrium constant $K_p = C_B C_C / C_A^2$ or

$$K_p = x_e^2 (1.5 - 2x_e)^2 = 16 \qquad \text{(V.43)}$$

Eq. (V.43) yields $x_e = 0.667$ kmole/m³. The amount of the reacted component A is $x_A = 0.8 \times 0.667 = 0.533$ kmole/m³. The final

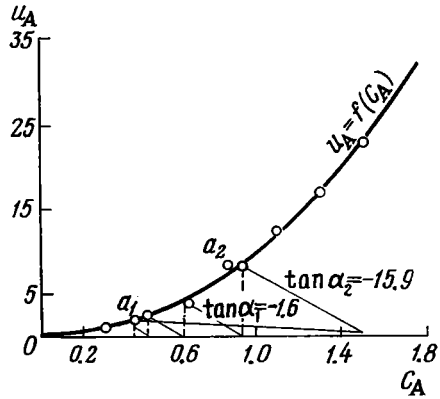


Fig. 15. Plot for calculating the parameters of a cascade of complete-mixing reactors (Problem 4).

concentration of A is $C_{A_f} = 1.5 - 2 \times 0.533 = 0.434$ kmole/m³.

According to the stoichiometric equation for the reaction the reaction rate is given by the equation

$$u_A = k_1 C_A^2 - k_2 C_B C_C = k_1 (C_A^2 - C_B C_C / K_p) \qquad \text{(V.44)}$$

or

$$u_A = 10 [(1.5 - 2x_A)^2 - x_A^2/16]$$

Figure 15 presents the function $u_A = f(C_A)$ plotted along the points with $C_A = 1.5$, 1.3, 1.1, 0.9, 0.7, 0.5, and 0.3 kmole/m³ and $u_A = 22.5$, 16.9, 12.1, 8.1, 4.9, 2.5, and 0.675 m³/kmole h, respectively.

Write down Eq. (V.27) for the mth reactor of the cascade:

$$\tau_m = v/V = (C_{A_{(m-1)}} - C_{A_m})/u_A \qquad \text{(V.45)}$$

For the first-order reactions the cascade of reactors can be described by Eq. (V.31). For more complicated reactions analytical description becomes too involved and we shall make use of the

graphical technique. Eq. (V.45) can be written as

$$u_A = \frac{C_{A(m-1)} - C_{Am}}{v/V} = -\frac{C_{Am} - C_{A(m-1)}}{\tau_m}$$

$$u_A = -\frac{1}{\tau_m}(C_{Am} - C_{A(m-1)}) \qquad (V.46)$$

The straight line corresponding to Eq. (V.46) with $C_{A(m-1)}$ intersects the plot of u_A in Fig. 15 at the point a_1. The slope of the straight line is

$$\tan \alpha_1 = -1/\tau_1 = -\Delta u/\Delta C = -1.7/(1.5 - 0.434) = -1.6$$

Hence, $\tau_1 = 0.627$ h for the one-stage process. The volume of the single reactor is

$$v = V\tau_1 = 10 \times 0.627 = 6.27 \text{ m}^3$$

Decrease the reactor volume by a factor of 10, that is, take $v = 0.627$ m^3. Then we have $\tau_m = 0.627/10 = 0.0627$ h and $\tan \alpha_2 = -1/\tau_m = -15.9$. The respective point of intersection of the curve $u_A = f(C_A)$ and the straight line $u_A = -\frac{1}{\tau_m}(C_{Am} - C_{A(m-1)})$ is a_2 in Fig. 15. It can be seen that 4 reactors are required to obtain the specified final concentration of A and the total volume of reactors is 2.5 m^3.

Problem 5. A batch-process reactor with an agitator produces 50 tons of ethyl acetate per day. The process is carried out at 100 °C in the liquid phase and is described by the equation

$$\underset{A}{C_2H_5OH} + \underset{B}{CH_3COOH} \rightleftarrows \underset{P}{CH_3COOC_2H_5} + \underset{Q}{H_2O}$$

The reaction rate is

$$u_A = k\left(C_A C_B - \frac{C_P C_Q}{K_p}\right) \qquad (V.47)$$

where $k = 7.93 \times 10^{-6}$ m^3/kmole and $K_p = 2.93$.

The starting aqueous solution has the density of 1020 kg/m^3 and contains 23% (by mass) of acetic acid and 46% of ethanol. The initial concentration of ethyl acetate is zero. The density of the reaction mixture remains constant throughout the process. The degree of conversion of the acid is 35%. The time needed for feeding the reactants to the reactor and discharging the products is 1 hour.

(1) Find the volume of the reactor.

(2) Find the productivity of the continuous-operation reactor of the same volume under the same process conditions.

(3) Find the reaction volume for a cascade of three complete-mixing reactors of the same productivity.

For simplicity the process is assumed to occur in the kinetic region under the isothermic conditions in all reactors.

Solution. 1. Batch-process reactor. Table 32 presents the calculated concentrations of the components in the starting, reaction, and final mixtures (x_B is the degree of conversion).

TABLE 32

Component	Molecular mass	Mixture			
		Starting		Reaction	Final
		kg/kg	kmole/m³	kmole/m³	kmole/m³
Ethanol (A)	46	0.46	10.2	$10.2-3.91\,x_B$	8.83
Acetic acid (B)	60	0.23	3.91	$3.91\,(1-x_B)$	2.54
Ethyl acetate (P)	88	0	0	$3.91\,x_B$	1.37
Water (Q)	18	0.31	17.56	$17.56+3.91\,x_B$	18.93

Eq. (V.6) yields the time of reaction for the batch-process reactor:

$$\tau = C_{B_1} \int_0^{x_{Bf}} dx/u_B$$

Let us express u_B as a function of x_B by substituting C_B expressed in terms of x_B in Eq. (V.47). That can be done because the molar reaction rates for the components are identical as can be seen from the stoichiometric reaction equation. We have

$$u_A = u_B = k\left[(10.2-3.91x_B)(1-x_B)\,3.91 - \frac{3.91x_B\,(17.56+3.91x_B)}{K_p}\right] \tag{V.48}$$

Substitution of Eq. (V.57) in Eq. (V.6) yields

$$\tau = C_{B_1} \int_0^{0.35} \frac{dx_B}{k\left[3.91\,(10.2-3.91x_B)\,(1-x_B) - \dfrac{3.91x_B\,(17.56+3.91x_B)}{K_p}\right]} \tag{V.49}$$

Eq. (V.49) is impossible to integrate exactly. Various approximation methods can be used for integration. We shall make use of the trapezoid rule:

$$\int_a^b y\,dx = \Delta/2\,(y_0 + 2y_1 + \ldots + 2y_{n-1} + y_n) \tag{V.50}$$

where $\Delta = (b-a)/n$ and n is the number of steps.

Eq. (V.49) can be written as

$$\tau = C_{B_1} \int_0^{0.35} y \, dx_B$$

where $y = 1/[k3.91\,(10.2 - 3.91x_B)\,(1 - x_B) - (3.91x_B/K_p)\,(17.56 + 3.91x_B)]$. If $n = 7$ we have $\Delta = 0.05$. For $x_B = 0$, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, and 0.35 we obtain $y_n = 3170$, 3470, 3750, 4440, 5150, 6010, 7360 and 9350, respectively. Thus Eq. (V.50) yields $\int_0^{0.35} y \, dx_B \approx 2$ h. Since the time of feeding the components and discharging the products is 1 hour the number of batches to be processed a day is $24/(2 + 1) = 8$.

The mixture of products contains 1.37 kmole/m³ of ethyl acetate so that the productivity of the reactor per day is $1.37 \times 88 \times 8 = 965$ kg/m³. Thus, to produce 50 tons of ethyl acetate a day the reactor should have the volume 50 000/965 = 52 m³.

2. Continuous-process reactor with complete mixing. Let us find the reaction rate for the mixture with final concentrations of components (see Table 32) which is found in the complete-mixing reactor. Eq. (V.47) yields

$$u_{B_f} = 7.93 \times 10^{-6}\,(8.83 \times 2.54 - 1.37 \times 18.93/2.93) =$$

$$= 1.075 \times 10^{-4} \text{ kmole/m}^3\text{s}$$

Since the factors of the stoichiometric equation are identical the magnitude of the molar rate of formation of ethyl acetate is equal to that of the rate of consumption of acetic acid. The molar rate of formation of ethyl acetate per 1 m³ of the reaction volume is $u_{P_f} = 88 \times 1.075 \times 10^{-4} = 9.46 \times 10^{-3}$ kg/m³ s. For the 52-m³ reactor the total productivity per day is $52 \times 9.46 \times 10^{-3} = 0.491$ kg/s = 42.4 tons per day, that is, the productivity is less than that of the batch-process reactor.

3. Cascade of three complete-mixing reactors. We shall use the approach described in the solution of Problem 4, that is, the graphical method since analytical solution for the reaction with kinetic equation (V.47) is too difficult.

Let us calculate the reaction rate (V.47) as a function of $C_B = 3.91\,(1 - x_B)$ (see Table 32). The results are given in Fig. 16 and the table below.

x_B	0.	0.05	0.1	0.15	0.20	0.25	0.30	0.35
C_B (kmole/m³)	3.91	3.72	3.52	3.33	3.14	2.94	2.74	2.55
$10^{-4} \cdot u_B$ (kmole/m³s)	3.16	2.88	2.67	2.25	1.94	1.66	1.36	1.07

Using the graphical method described in Problem 4 we plot three similar rectangular triangles between the concentrations C_{B_i} and C_{B_f}. We obtain $\tan \alpha = 1/\tau_n = 3.5 \times 10^{-4}$ and $\tau_n = 2860$ s. The final concentration of ethyl acetate is 1.37 kmole/m³ = 88 × 1.37 = = 120 kg/m³. The flow rate in the cascade of reactors producing

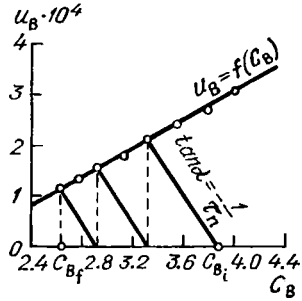


Fig. 16. Plot for calculating the volume of one reactor in a cascade (Problem 5).

50 tons of ethyl acetate a day is $V_m = 50\,000/24 \times 3600 \times 120 = = 4.83 \times 10^{-3}$ m³/s. The time of residence of the reaction mixture in the nth reactor with the volume v is

$$\tau_n = v/V_m$$

Hence we obtain $v = \tau_n V_m = 2.86 \times 10^3 \times 4.83 \times 10^{-3} = 14$ m³. Thus, the total volume of the cascade of three reactors is 42 m³, that is, it is much smaller than the volume of the batch-process reactor with the same productivity.

Further Problems for Students

1. Find the volumes of the ideal plug-flow reactor and the complete-mixing reactor for oxidation of SO_2 to SO_3 over the vanadium catalyst for the degrees of conversion of 0.3 and 0.7. The process is carried out at the constant temperature of 569 °C. The reaction rate is given by the equation

$$u = (k/2a)\,[(x_e - x)/x]^{0.8}\,(2b - ax)$$

where a and b are the initial concentrations of SO_2 and O_2 (% by volume) in the reaction mixture. The gas flow rate is 10 000 m³/h. The initial gas mixture has the following composition (% by volume): SO_2—9, O_2—10, N_2—81. The reaction rate constant is 11 at 569 °C. The equilibrium yield is $x_e = 0.79$.

2. The second-order reaction between 0.0121 N solution of ethyl acetate and 0.0462 N solution of sodium hydroxide fed with the flow rates of 3.12 and 3.14 litres/s is carried out in a 6-m³ complete-mixing reactor. The reaction rate constant is 0.11 m³/mole s. Calcu-

late the concentration of ethyl acetate in the mixture of products for the steady-state process and the amount of reacted ethyl acetate.
3. A second-order reaction is carried out in the solution. The concentrations of the reactants are equal. The required degree of conversion is 90%. The reaction time for the batch-process reactor is 7 min. Calculate the residence time for the components in the cascade of two and three reactors.
4. A solution of a component with the concentration C_2 is fed with the flow rate V'_m to a reactor which contains v m^3 of the solution of another component with the concentration C_1. The rate of flow of the mixture discharged from the reactor is V''_m. The reaction mixture is intensively mixed so that the concentration is uniform over the reactor volume and is equal to the concentration of the mixture discharged from the reactor. The rate of the reaction occurring in the reactor is $u = kC^n$. Calculate the material balance for the process.

Chapter VI

Heterogeneous Catalytic Processes

Introduction

The phenomenon of *catalysis* is variation of the reaction rates or initiation of reactions which is caused by the action of special substances, catalysts, which enter into the reaction forming intermediate compounds with the reactants but return to the original composition by the end of the catalytic process.

If the catalyst accelerates a reaction it is known as the *positive* catalyst and if it inhibits a reaction it is referred to as the *negative* catalyst. Chemical industries make use mostly of the positive catalysis which will be discussed in this chapter.

The catalytic effect is highly specific and it is essentially different from the effects of other factors which influence process rates, such as temperature, pressure, initial concentrations of reactants, degree of mixing, and so on. For instance, a universal method for intensification of processes is the increase in temperature which raises the reaction rate constants and the mass-transfer coefficients. However, the temperature cannot be increased above a limit determined by the heat resistance of reactor materials and by displacement of the equilibrium resulting in decrease of the driving force of exothermic reversible processes. In contrast, catalytic promotion of reactions has no limitations and can be highly effective as it can increase the reaction rates by a factor of millions. The activation energies of reactions decrease in the presence of catalysts owing to the changes in the reaction mechanisms.

In the presence of catalyst the reaction passes a number of intermediate stages with lower activation energies than those of the non-catalytic reaction. For instance, the bimolecular reaction

$$A + B \rightarrow AB$$

can proceed via the following intermediate stages in the presence of catalyst Cat:

$$A + [Cat] = A[Cat] \quad (a)$$

$$A[Cat] + B = AB^*[Cat] \quad (b)$$

$$AB^*[Cat] = AB + [Cat] \quad (c)$$

Figure 17 shows variation of the energy of a reacting system in a non-catalytic reaction (curve *1*) and in the presence of catalyst (curve *2*). The activation energy of the non-catalytic reaction is E,

the activation energy of the catalytic reaction (at the limiting stage) is E_c, and E_1 and E_2 are the activation energies of the stages (a) and (b). The reaction rate constant increases with decreasing E according to the Arrhenius equation (IV.27) $k = k_0 \exp(-E/RT)$ and owing to the exponential relationship the increase of E can be fairly large even for a small decrease* of E. In some cases the decrease of the activation energy is accompanied by a decrease

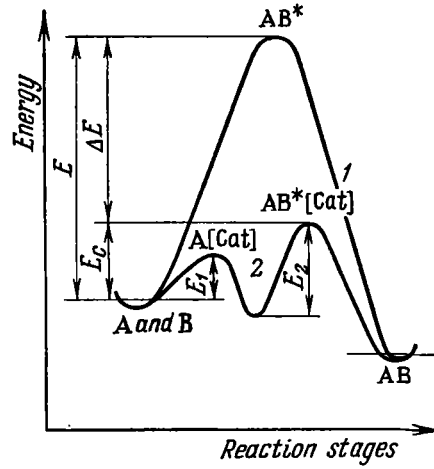


Fig. 17. Variation of the energy of the reacting system in non-catalytic (curve *1*) and catalytic (curve *2*) reactions.

in the reaction order since the order of the elementary stages of the catalytic reaction can be lower than the order of the non-catalytic reaction.

The catalytic processes and reactions can be classified by various characteristics. Depending on the phase state of the reactants and the catalyst the catalytic processes are classified into two groups—*homogeneous* and *heterogeneous* processes.

In homogeneous processes the catalysts and reactants are in the same phase state—gas or solution, while in heterogeneous processes they are in different phase states. A special group comprises micro-heterogeneous catalytic process, in particular, the enzyme catalysis which occurs in the liquid phase with colloid particles acting as catalysts.

Depending on the type of interaction between catalysts and reactants catalytic reactions can be classified into two groups—those with the *reduction-oxidation* (homolytic) interaction and those with the *acid-base* (heterolytic) interaction. The reduction-oxidation

* In some catalytic reactions the decrease of E is accompanied by a decrease of the pre-exponential factor k_0 so that the overall increase of the reaction rate in the presence of catalyst is lower than the calculated value. However, for considerably lower E the effect of decreasing k_0 is not significant.

catalysts are the transitional metals and oxides of metals with variable valence. The general mechanism of the reduction-oxidation catalysis is based on electron exchange between catalyst and reactants facilitating electron transitions in the reacting molecules. The mechanism of the acid-base catalysis consists in exchange of protons or ions (anions and cations) between catalyst and reactants. Typical catalysts of this class are acids (donating H^+) and bases (donating OH^-).

The *selective* catalysis consists in promotion of only one of several possible (consecutive or simultaneous) reactions. Selective catalysis is especially useful in industrial applications. Various products can be manufactured from the same starting materials by making use of selective catalysts. Selective catalysts can be applied to accelerate sharply one reaction of a number of possible reactions so that the process can be carried out at a low temperature and other reactions can be inhibited.

The type of catalysis most widely used in chemical industry is the heterogeneous catalysis with solid catalysts. The heterogeneous catalytic process proceeds via the mass exchange and chemical stages which can be generally described as follows: (1) diffusion of reactants from the flow core to the surface of the catalyst particles; (2) diffusion in the pores of catalyst particles; (3) activated (chemical) adsorption of reactants on the catalyst surface and formation of surface compounds; (4) rearrangement of atoms and formation of product-catalyst complexes at the surface; (5) desorption of the product (regeneration of the active centres of catalyst); (6) diffusion of the product in the pores of catalyst particle; and (7) diffusion of the product from the surface of catalyst particle to the flow core.

The overall rate of a heterogeneous catalytic process is determined by that of its slowest stage (s). According to the limiting process stage the processes are classified as being limited by the *kinetics*, *external diffusion*, and *internal diffusion*.

Generally, the rate constant of a catalytic process can be written as

$$k = f(k_1, k_2, k_{side} \ldots D_m, D'_m, D_p) \qquad \text{(VI.1)}$$

where k_1, k_2, k_{side} are the rate constants of the direct, reverse, and side reactions and D_m, D'_m, D_p are the diffusion coefficients of the starting materials and products for the processes limited by external or internal diffusion. For the processes limited by kinetics the rate constant is independent of the diffusion parameters.

According to the hydrodynamical interaction between the gas flow and particulate catalyst the catalytic reactors are classified into the following groups: (1) reactors with *stationary* (*filter*) *bed* of catalyst; (2) reactors with *fluidized bed* of catalyst; and (3) reactors with catalyst *continuously moving* along the reaction space.

This classification does not include the surface-contact heterogeneous catalytic reactors in which gas is passed through catalyst piping or netting.

Depending on the temperature conditions the catalytic processes and reactors can be classified as *adiabatic*, *isothermic*, and *variable-temperature* ones. The reactors with filter catalyst bed whose hydrodynamics are close to ideal plug flow operate under adiabatic or variable-temperature conditions. The fluidized-bed reactors typically operate under isothermic conditions.

The main technological parameters of the heterogeneous catalytic process which must be specified or calculated are the degree of conversion x, the catalyst activity A_{cat}, the catalyst selectivity S_{cat}, the reaction rate constant k, the time τ of contact between reactants and catalyst, the gas flow rate V_g in the catalyst bed, the catalyst productivity P_{cat}, the catalyst intensity i_{cat}, the catalyst poisoning coefficient α, the optimum temperature T_{opt}, and others.

Apart from the above parameters we should calculate the dimensions of the reactor including the height of the catalyst bed, the hydraulic resistance ΔP of the filter or fluidized bed, the critical rate of suspension of the solid particles and other hydrodynamic parameters, the heat-exchange surface area F for heat removal from the catalyst bed (or delivery of heat to the reactor), and so on.

For the catalytic reactions in which the pre-exponential factor k_0 in Arrhenius equation (IV.27) is not changed by the presence or absence of catalyst the activity of catalyst can be measured by the ratio of the rate constant k_{cat} of the catalytic reaction to the rate constant k of the non-catalytic reaction:

$$A_{cat} = k_{cat}/k = e^{-E_{cat}/RT}/e^{-E/RT} = e^{\Delta E/RT} \qquad \text{(VI.2)}$$

Here $\Delta E = E - E_{cat}$ is the decrease of the activation energy of the catalytic reaction compared with the non-catalytic reaction.

To compare the activities of catalysts under different conditions the activity is determined as the intensity of process with a given catalyst expressed in kg/m³ h:

$$A'_{cat} = G_p/v_{cat}\tau \qquad \text{(VI.3)}$$

Here G_p is the amount of the product, v_{cat} is the volume of the catalyst, and τ is the time of reaction. Another measure of activity is

$$A''_{cat} = G_p/G_{cat}\tau \qquad \text{(VI.4)}$$

and

$$A_{sp} = G_p/S\tau = G_p/S_{sp}v_{cat}\tau \qquad \text{(VI.5)}$$

where G_{cat} is the amount of catalyst, S is the total surface of the catalyst, and S_{sp} is the specific surface area of the catalyst, m²/m³.

The productivity $P_{cat} = G_p/\tau$ and the intensity of operation i of the catalyst (in kg/m³ h) are related to the catalyst activity:

$$i = V_{v_f} C_p \rho_p \tag{VI.6}$$

or

$$i = V_{v_i} C_m x \rho_p \beta \tag{VI.7}$$

Here C_p and C_m are the concentrations of the product and the main starting material (molar fractions), ρ_p is the density of the product (kg/m³), V_v is the volume rate of flow of the gas (1/h) which is the ratio of the flow rate V_g (m³/h) to the catalyst volume v (m³):

$$V_v = V_g/v \tag{VI.8}$$

and the factor $\beta = V_{v_f}/V_{v_i}$ is used to convert the initial V_{v_i} into the final V_{v_f} to allow for variation of the volume of the reaction mixture.

The catalyst selectivity S_{cat} is defined as the ratio between the rate of formation of the specified main product and the overall rate of conversion of the main starting reactant in all reactions:

$$S_{cat} = \frac{dG_p}{\frac{\nu_p}{\nu_i}(dG_i)} \tag{VI.9}$$

Here ν_p/ν_i is the ratio of the stoichiometric factors for the formation of product from the main initial reactant.

The overall (integral) selectivity can be expressed as

$$S_{cat} = G_m/G = G_m/(G_m + G_s) \tag{VI.10}$$

where G_m is the amount of the main product and G_s is the amount of the side products. The selectivity is sometimes expressed in percentages.

The time of residence τ in the catalytic reactors with the ideal plug flow is the same for all molecules. The theoretical residence time is

$$\tau_{th} = v'_{cat}/V_g = H/w \tag{VI.11}$$

where v'_{cat} is the total volume of the catalyst (m³), V_g is the gas flow rate (m³/h), H is the height of the catalyst bed; and w is the linear velocity of the gas in the reactor (m/h).

The real residence time is

$$\tau_r = \tau_{mean} = \tau_{th}/\varepsilon \tag{VI.12}$$

where $\varepsilon = v_f/v_{cat}$ is the porosity of the catalyst bed and v_f is the free volume of the bed (m³). The time of residence is found from the kinetic equations (see Chapter IV, Introduction).

In the complete-mixing reactor the time of residence in the reactor for individual molecules can theoretically vary from 0 to infinity, that is $\tau \neq \tau_{mean}$. The time τ is calculated from the kinetic equations for the complete-mixing conditions when C, ΔC, and x are constant throughout the reaction volume (see Chapter V, Introduction).

The catalyst volume needed to obtain a given degree of conversion is found from

$$v_{cat} = cV_g\tau_{th} \qquad \text{(VI.12a)}$$

where c is the reserve factor which allows for a decrease of the catalyst activity owing to poisoning and mechanical losses, V_g is the gas flow rate, and τ_{th} is the theoretical time of contact between the gas and the catalyst.

Calculations of Catalytic Reactors

The general kinetic equations provide a basis for calculations of the parameters of catalytic reactors. Chapters IV and V of this book deal in detail with the kinetic equations of various reactions and for chemical reactors of various types. All these can be modified to calculate the parameters of the catalytic processes.

If the specific surface S_{sp} (in m^2/m^3) of the catalyst is known we have for the plug-flow reactors

$$u = dG/d\tau = kv_{cat}\, S_{sp}\Delta C \qquad \text{(VI.13)}$$

where k is the overall reaction rate constant and ΔC is the driving force of the process. The general kinetic equation for the catalytic reaction of gas reactants over the solid catalyst taking into account the main process parameters can be written as

$$u = k_0 e^{-E/RT} v_{cat} \Delta p P^n \beta \qquad \text{(VI.14)}$$

where Δp is the driving force of the process expressed in terms of the partial pressures of the reactants, P is the ratio of the process pressure to the normal pressure (1.01×10^5 Pa), β is the factor for conversion to normal temperature, and n is the overall reaction order.

Depending on the limiting stage of the process the kinetic equations for heterogeneous catalytic processes over the solid porous catalysts can be written in various forms.

(1) For the processes limited by external diffusion the overall mass transfer equation can be written as

$$u = \frac{1}{S}\frac{dG_p}{d\tau} = k_M (C_{A_g} - C^*_{A_g}) \qquad \text{(VI.15)}$$

where S is the surface of contact between reactants and catalyst; C_A is the concentration of the main reactant A in the gas (kmole/m^3), $C^*_{A_g}$ is the equilibrium concentration of A near the surface of the catalyst; and k_M is the mass-transfer coefficient. The concentration $C^*_{A_g}$ is not known and should be eliminated. The coefficient k_M for various conditions can be found in literature or measured experimentally.

The dimensions of the reactor are sometimes determined by calculating the values of the height of transfer unit (HTU) and the number Z of transfer units:

$$H = \text{HTU}\, Z \tag{VI.16}$$

Here we have

$$\text{HTU} = \frac{G_g}{M_m k_M S_{sp} p_m} \tag{VI.17}$$

where G_g is the mass flow rate of the gas (kg/m^2 h), M_m is the mean molecular mass of the gas components, k_M is the mass-transfer coefficient (for the component A) (kmole/m^2 h Pa), S_{sp} is the specific surface of the catalyst (m^2/m^3), and p_m is the mean logarithmic partial pressure of the component A in the gas film

$$p_m = \frac{(P + p_A\beta_A) - (P + p_{A_1}\beta_A)}{\ln \dfrac{P + p_A\beta_A}{P + p_{A_1}\beta_A}} \tag{VI.18}$$

In Eq. (VI.18) P is the pressure in the reactor (Pa), p_A is the partial pressure of the component A (Pa), p_{A_1} is the partial pressure of A at the catalyst surface (Pa), and β_A is the change of the number of moles of A owing to the reaction (per 1 mole of A).

The HTU value is sometimes found from the empirical equations of the following type:

$$S_{sp}\text{HTU} = B\,\text{Re}^m\,(\text{Pr}')^n \tag{VI.19}$$

Here we have

$$\text{Re} = d_{cat} G_g / \rho D \text{ and } \text{P}'_r = \mu / \rho D$$

Here d_{cat} is the reduced diameter of the catalyst particles, D is the diffusion coefficient of the component A in the gas, μ and ρ are the viscosity and the density of the gas for the given P and T in the reactor. The number of transfer units is

$$Z = \int_{p_{A_2}}^{p_{A_1}} \frac{p_m\, dp_A}{(P + p_A\beta_A)(p_A - p_{A_1})} = \int_{N_{A_2}}^{N_{A_1}} \frac{N_m\, dN_A}{(1 + N_A\beta_A)(N_A - N_{A_1})} \tag{VI.20}$$

where N_A and N_{A_1} are the molar fractions of the component A in the gas and at the surface of the catalyst and $N_m = p_m/P$ is the mean logarithmic concentration of A in the gas film.

The number of transfer units Z can be found by approximate graphical integration of Eq. (VI.20) using a plot of p_A as a function of $p_m/(P + p_A\beta_A)(p_A - p_{A_1})$ or by analytical techniques with various simplifying approximations.

(2) For the kinetics-limited processes the form of the equation depends on the limiting stage of the surface interaction. For instance, if the limiting stage of the gas reaction occurring in the presence of a neutral material

$$A + B \rightleftarrows R + S$$

is adsorption of A at the catalyst surface the kinetic equation is

$$-u_A = \frac{k\left(p_A - \frac{p_R p_S}{K_p p_B}\right)}{1 + K_R K_S p_R p_S + K_B p_B + K_R p_R + K_S p_S + K_{in} p_{in}} \qquad \text{(VI.21)}$$

If the limiting stage is the surface interaction between the adsorbed molecules A and B the equation can be written as

$$-u_A = \frac{k\left(p_A p_B - \frac{p_R - p_S}{K_p}\right)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_{in} p_{in})^2} \qquad \text{(VI.22)}$$

and if the limiting stage is desorption we have

$$-u_A = \frac{k\left(\frac{p_A p_B}{p_S} - \frac{p_R p_S}{K_p}\right)}{1 + K_A p_A + K_B p_B + K_p p_A \frac{p_B}{p_S} + K_{in} p_{in}} \qquad \text{(VI.23)}$$

In Eqs. (VI.21)-(VI.23) k is the reaction rate constant; K_p is the equilibrium constant for the surface reaction; K_A, K_B, K_R and K_S are the equilibrium constants for adsorption of the initial components of the gas mixture and the reaction products, K_{in} is the equilibrium constant for adsorption of the inert substance.

(3) If the reaction is limited by internal diffusion the mean reaction rate for the first-order or pseudomonomolecular reaction inside the pore is

$$u = -\frac{1}{S_p} \cdot \frac{dG_A}{d\tau} = k_S C_{A_T} \gamma \qquad \text{(VI.24)}$$

or

$$u = -\frac{1}{v_p} \cdot \frac{dG_A}{d\tau} = k C_{A_T} \gamma \qquad \text{(VI.25)}$$

Here S_p and v_p are the surface and volume of the pore, k_S is the reaction rate constant per unit surface area of the catalyst (m/h),

k is the reaction rate constant (1/h), $\gamma = \bar{C}_A/C_{A_T}$ is the factor characterizing the degree of utilization of the internal surface of the pore, $\bar{C}_A$ is the mean concentration of A inside the pore and C_{A_g} is the highest possible concentration of A near the catalyst surface.

The overall rate of the catalytic process for the first-order reaction is found by combining the equation for the mass-transfer rate

$$u = -\frac{1}{S}\frac{dG_A}{d\tau} = k_M (C_{A_g} - C^*_{A_g})$$

with the equation for diffusion and reaction inside the catalyst particle

$$u = -\frac{1}{v_p}\frac{dG_A}{d\tau} = kC^*_{A_g}\gamma$$

Elimination of the unknown surface concentration $C^*_{A_g}$ yields

$$u = -\frac{1}{S}\frac{dG_A}{d\tau} = \frac{1}{\frac{S}{k\gamma v_p} + \frac{1}{k_M}} C_{A_g} \qquad \text{(VI.26)}$$

or

$$u = -\frac{1}{v_p}\frac{dG_A}{d\tau} = \frac{1}{\frac{1}{k\gamma} + \frac{v_p}{k_M S}} C_{A_g} \qquad \text{(VI.27)}$$

(here k is given in 1/h and k_M in m/h).

For instance, for the spherical catalyst particles with the radius r we obtain

$$u = -\frac{1}{S}\frac{dG_A}{d\tau} = \frac{1}{\frac{3}{k\gamma r} + \frac{1}{k_M}} C_{A_g} \qquad \text{(VI.28)}$$

The kinetic equations in combination with the heat and material balances yield the main parameters of the catalytic reactors. Other important characteristics which should be calculated are the hydrodynamic parameters of the reactors and the surfaces of the heat exchangers.

The reactors with fluidized, filter and moving catalyst beds are described by similar kinetic, heat-exchange and mass-exchange equations. The kinetic equations for the fluidized-bed reactors differ from those for the filter-bed reactors only in the magnitudes of the equation terms. For instance, the value of k in the isothermal fluidized-bed reactor can be 3-10 times that in the adiabatic filter-bed reactor and the effective catalyst surface is also larger. In the fluidized-bed reactor the driving force ΔC of the process can be considerably lower owing to mixing than in the filter-bed reactor with an almost ideal plug flow. The higher are the degree of conversion and

the order of the catalytic reaction the larger is the decrease of ΔC. For low degrees of conversion and first-order or pseudo-monomolecular reactions (which is often found for catalytic reactions) the fluidized-bed and filter-bed reactors have close values of ΔC.

The principal hydrodynamic parameters of the fluidized-bed reactor are, primarily, those that determine the range of existence of the fluidized bed, that is, the critical rates of suspension and removal of the catalyst particles. Another significant parameter is the hydraulic resistance ΔP of the bed.

The rate w_{susp} of suspension when it begins can be found from the formula

$$Re_{susp} = Ar\,(1400 + 5.22\sqrt{Ar}) \qquad (VI.29)$$

where $Re_{susp} = w_{susp}d_{cat}/\nu$ and $Ar = gd_{cat}(\rho_T - \rho_g)/\nu^2\rho_g$. Here d_{cat} is the diameter of the catalyst particles (m), ν is the kinematic viscosity (m^2/s), ρ_T and ρ_g are the densities of the catalyst and the gas mixture, and g is the acceleration of gravity.

The real rate of the beginning of suspension is given by

$$w_{real} = w_{susp}/\varepsilon \qquad (VI.30)$$

where ε is the porosity of the catalyst bed.

The suspension (fluidization) number is

$$W = w/w_{susp} \qquad (VI.31)$$

where w is the operating (actual) velocity of the gas.

Eq. (VI.29) yields w_{susp} with an accuracy which is sufficient for engineering purposes. A wider range of rates is given by the equation

$$w_{real} = 0.5\sqrt{(94\nu/d)^2 + 3.7\rho_T d/\rho_g} - 47\,\nu/d \qquad (VI.32)$$

The gas velocity w_{rem} corresponding to removal of the catalyst particles can be found from the equation

$$Re_{rem} = \frac{Ar_{min}}{18 + 0.6\sqrt{Ar_{min}}} \qquad (VI.33)$$

where Ar_{min} is determined for the smallest catalyst particles with the smallest diameter d_{min}.

The values of the ratio w_{rem}/w_{susp} determine the range of existence of the fluidized bed:

$$w_{rem}/w_{susp} = (1400 + 5.22\sqrt{Ar})/(18 + 0.6\sqrt{Ar}) \qquad (VI.34)$$

For low Ar values (small particles) we have $w_{rem}/w_{susp} \to 80$ and for high Ar values (large particles) $w_{rem}/w_{susp} \to 8$.

For the catalyst particles with $d_{cat} = 0.2$-4 mm which are typically used in the catalytic reactors $w_{rem}/w_{susp} = 10$-15.

Calculations of the heat-exchange surface area F which is needed to remove (deliver) the heat from the catalyst bed are made according to the general heat-transfer equation

$$Q = k_T F \Delta t \tau \tag{VI.35}$$

The driving force Δt of heat transfer is determined by the temperature t_{bed} in the bed and the temperature t_{cool} of the cooling agent. Owing to mixing the heat transfer in the fluidized bed from the catalyst particles to the heat-exchange surface (or in the reverse direction) is highly intensive so that the process is isothermal across and along the bed.

If the adiabatic reactor with filter catalyst bed has no heat exchangers the final temperature t_f of the reaction mixture can be found from the given initial temperature t_i:

$$t_f = t_i + q_r C_p x / \bar{c} \tag{VI.36}$$

here q_r is the heat effect of the reaction (J/mole), C_p is the product concentration in the reaction mixture, $\bar{c}$ is the mean specific heat of the reaction mixture (J/mole K), and x is the degree of conversion.

The heat-transfer coefficient k_T is given by

$$k_T = 1/(1/\alpha_1 + 1/\alpha_2 + \delta_w/\lambda_w) \tag{VI.37}$$

where δ_w is the wall thickness of the heat exchanger, λ_w is the heat conductivity of the heat-exchanger wall, and α_1 and α_2 are the convective heat-transfer coefficients.

In filter-bed reactors it is typically necessary to determine the dimensions of the heat exchangers outside the catalyst beds which remove heat between catalysis stages. This is done by calculating the heat flows, temperature field in the reactor, and so on.

The heat exchangers in the fluidized-bed reactors are located inside the catalyst beds owing to their isothermal conditions so that the heat is removed (or delivered) in the course of the catalytic process. For these reactors Eq. (VI.37) is transformed into

$$k_T = 1/(1/\alpha_{susp} + \delta_w/\lambda_w + 1/\alpha_{cool}) \tag{VI.38}$$

where α_{susp} is the coefficient of the convective heat transfer from the fluidized bed to the heat-exchanger surface and α_{cool} is the coefficient of the convective heat transfer from the heat-exchanger wall to the cooling agent.

The heat-transfer coefficient in the fluidized bed is much higher than that in the stationary bed. For the high-turbulence regime the highest value of α_{susp} corresponding to the optimum gas velocity $w_{g_{opt}}$ is found from the following equation:

$$Nu_{max} = 0.86 Ar^{0.2} \tag{VI.39}$$

When $w_g < w_{g_{opt}}$ we have

$$Nu = 0.08Re^{0.65}Ar^{0.1} \quad (VI.40)$$

Here

$$Nu = \alpha_{susp} d_{cat}/\lambda_g \text{ and } Ar = g d_{cat}^3 (\rho_T - \rho_g)/\nu^2 \rho_g$$

and λ_g is the heat conductivity of the gas.

Some special calculations have to be made for the reactors with a moving catalyst which are used mainly for endothermic processes. One parameter to be calculated is the initial temperature of the catalytic process in the zone of high-intensity heat exchange between the hot particles of the catalyst and the reactants (typically, the steam-gas mixture). Owing to high turbulence of the flows the temperatures in the lower part of the reactor where the flows meet are rapidly equalized and a certain initial temperature of the process is established.

The *hydraulic resistance* of the filter catalyst bed is given by

$$\Delta P = \xi H S \rho w_{th}^2/8\varepsilon_0^3 \quad (VI.41)$$

where ξ is the resistance coefficient, H is the height of the bed (m), S is the specific surface of the catalyst particles (m^2/m^3), ρ is the gas density (kg/m^3), w_{th} is the theoretical gas velocity (m/s), and ε_0 is the porosity of the stationary bed. For $Re < 50$ we have $\xi = 220/Re$ and $\xi = 11.6/Re^{0.25}$ for $Re > 50$.

The hydraulic resistance ΔP of the fluidized bed is found from the condition for the existence of the fluidized bed, that is, by equating the hydrodynamic pressure to the gravity for the particles. Hence, for the bed with the height H we obtain

$$\Delta P = g\rho_T (1 - \varepsilon) H \quad (VI.42)$$

where ρ_T is the density of the catalyst particles and ε is the mean porosity of the fluidized bed (under process conditions).

A sufficiently accurate approximation of Eq. (VI.42) is

$$\Delta P = g\rho_b H_0 \quad (VI.42a)$$

where ρ_b is the bulk density of the catalyst particles (kg/m^3) and H_0 is the height of the bed at rest (m).

The height H of the fluidized bed is given by

$$H = H_0 (1 - \varepsilon_0)/(1 - \varepsilon) \quad (VI.43)$$

The porosity of a non-uniform fluidized bed is often expressed in terms of the numbers Ar and Re:

$$\varepsilon = ((18Re + 0.36Re^2)/Ar)^{0.21} \quad (VI.44)$$

Calculations of the parameters of a catalytic reactor should be carried out according to a specified procedure. Below, we shall describe the procedure for calculating the parameters of the multibed reactor used for conducting a reversible exothermic process in the gas phase over a solid catalyst.

1. Compile a tentative table of yields and temperatures at the beds (or plot the x *vs.* t diagram). Calculate the equilibrium constants, find the equilibrium yield $x_e = f(K_p)$, and plot the equilibrium curve (see also Chapters II and IV). Calculate the optimum temperatures for each stage of the process and plot the curve of optimum temperatures (Eqs. (IV.15) and (IV.32); see Chapter IV, Problem 11).

2. Calculate the material balance (see Chapter I) for the reactor as a whole and for the catalysis stages (reactor beds) using the x *vs.* t diagram. Find the flow rates for the gas mixture and its components at the entrance, each bed and exit of the reactor.

3 (for the fluidized-bed reactors). Calculate the hydrodynamic parameters of the reactor, evaluate the catalyst particle diameters and select the optimum one, calculate the critical gas velocities for the formation of the fluidized bed and removal of catalyst particles (Eqs. (VI.29)-(VI.34)), and find the operational gas velocity in the reactor.

4. Find the volume v_{cat} of the catalyst for the reactor as a whole and for the individual beds using the general kinetic equations (VI.13) and (VI.14) (for instance, Eqs. (V.14), (V.26) and (V.27)). The reaction rate constant can be found from Eqs. (IV.27) and (IV.28). Then calculate or determine with a graphical technique (see Chapter V) the time τ of contact between the gas and the catalyst for each bed (or for the reactor) which is needed to obtain the specified product yield x. From the known time τ and the material balance data find the catalyst volume v_{cat} taking into account the reserve factor c which is usually obtained from practical experience.

5. Calculate the main dimensions of the reactor, that is, the cross-section area S, the internal diameter D, and the height of the stationary catalyst bed H_0 from the material balance data (the flow rate V_g), the operational gas velocity w_g, the catalyst volume v_{cat}, and the optimum temperatures T_{opt}.

6. Find the hydraulic resistance of the catalyst beds and the reactor using Eqs. (VI.41)-(VI.44).

7. Calculate the heat balances for the reactor beds and find the surface areas of the heat exchangers in the catalyst beds (for the fluidized-bed reactors) which remove heat from the bed (see Eqs. (VI.38)-(VI.40)).

Calculations of the Parameters of Catalytic Processes and Reactors

Problem 1. Determine the productivity of 1 m^3 of the catalyst for ammonia synthesis which is carried out under the following conditions. The ammonia concentration in the discharged product mixture $C_f = 26.5\%$ by volume, the ammonia concentration in the starting mixture $C_1 = 2.7\%$ by volume. The gas flow rate $V_g = 45\,000$ m^3/h per 1 m^3 of the catalyst.

Solution. Ammonia synthesis is an exothermic reversible reaction with decreasing volume:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 + q$$

The ammonia synthesis reaction requires a high activation energy. The industrial process is carried out in the presence of catalyst under a high pressure increasing the equilibrium degree of conversion and at a high temperature which provides for a sufficiently high process rate but shifts somewhat the equilibrium towards the starting components. The catalyst for ammonia synthesis is iron activated by K_2O, Al_2O_3, SiO_2, and CaO. However, even the optimum conditions provide only for a low ammonia yield (x = 18-22% by volume) and therefore the process is carried out with recycling.

The recycled gas fed to the synthesis column after condensation of ammonia contains residual ammonia and the added fresh nitrogen-hydrogen mixture compensates for the reacted material and the process losses.

The ammonia yield is determined by the ammonia content in the mixture of products. In our case we have

$$x = (C_f - C_1)/(100 + C_f) = (26.5 - 2.7)/102.7 = 23.2\%$$

by volume or 0.232 molar fraction.

The productivity P of the catalyst in the ammonia synthesis column (in kg/h per 1 m^3 of catalyst) for a given pressure and a given composition of the nitrogen-hydrogen gas is found from the formula similar to Eq. (VI.6):

$$P = 0.771 x V_g \beta \qquad \text{(VI.45)}$$

Here 0.771 (kg) is the mass of 1 m^3 of NH_3 and β is the factor describing the decrease of the gas volume in the synthesis reaction

$$\beta = (100 + C_1)/(100 + C_f) = (100 + 2.7)/(100 + 26.5) = 0.81 \qquad \text{(VI.46)}$$

Hence, we obtain P = 6500 kg/h per 1 m^3 of catalyst.

Problem 2. Find the catalyst volume v_{cat} in the ammonia synthesis column and the time τ of contact between the gas and the catalyst. The reactor productivity is 96 tons of ammonia per day, the pres-

sure $P = 800 \times 1.01 \times 10^5$ Pa, the temperature $t = 500$ °C, the gas flow rate is $V_v = 60\,000$ m³/h per 1 m³ of catalyst. The product yield is $x = 20\%$. The free volume v_f of the catalyst is 30% of its total volume. Consumption of the nitrogen-hydrogen mixture is 3000 m³ per 1 ton of ammonia. To simplify calculations the impurities in the gas (Ar, CH_4) are ignored.

Solution. The reactor productivity is $P = 96/24 = 4$ tons/h. The flow rate of the recycled gas taking into account the product yield is approximately $V_g = 4 \times 3000/0.2 = 60\,000$ m³/h. Hence, the catalyst volume is $v_{cat} = V_g/V_v = 1$ m³.

The reaction volume V_r of the gas (under the reaction conditions) can be found if we know the compressibility f of the nitrogen-hydrogen mixture:

$$f = PV_r/P_0V_0$$

The values of f for various temperatures and pressures can be found in handbooks*. For our conditions, that is the pressure of 8×10^7 Pa and the temperature of 500 °C we can find $f = 3.5$ by extrapolating the values for the lower temperatures since compressibility varies almost proportional to t. Hence, we find

$$V_r = fP_0V_0/P = 3.5 \times 9.81 \times 10^4 \times 60\,000/8 \times 10^7 = 264 \text{ m}^3/\text{h}$$

The time of contact between the gas and the catalyst is given by Eqs. (VI.11)-(VI.12a):

$$\tau = v_f \times 3600/V_r = 1 \times 0.3 \times 3600/264 = 4.1 \text{ s}$$

Problem 3. The process of methanol oxidation into formaldehyde over a selective solid oxide catalyst is studied in a laboratory reactor with recycling of the reaction mixture after removal of the product. The rate of circulation of the mixture (with a pump) is much higher than the rates of feeding of the reactants and removal of the products. The degree of conversion in one cycle is very small compared with the overall yield. Oxidation of methanol involves the following irreversible reactions:

$$CH_3OH + 0.5O_2 = CH_2O + H_2O \quad (1)$$

$$CH_2O + 0.5O_2 = CO + H_2O \quad (2)$$

The gas flow rate is $V_g = 10$ litres/h, the catalyst volume is $v_{cat} = 5$ cm³. The initial concentration of methanol in the methanol-air mixture is $C_{meth} = 6.5\%$ by volume. The overall degree of conversion of methanol is $x_1 = 0.98$ and the yield of formaldehyde is $x_2 = 0.9$. Calculate the rate constants of reactions (1) and (2) in the presence of the selective catalyst.

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* See, for instance, E. Blasyak *et al.*, *Technology of Bound Nitrogen*, Goskhimizdat, Moscow, 1961, p. 460 (in Russian).

Solution. The degree of conversion and the reaction rate can be assumed uniform throughout the reactor. The reaction rates are given by Eq. (IV.1):

$$u_1 = k_1 \Delta C_1 \quad \text{and} \quad u_2 = k_2 \Delta C_2$$

The irreversible reactions of oxidation of methanol and formaldehyde can be regarded as pseudomonomolecular reactions since one of the reactants (oxygen of the air) is present in a large excess. Hence, we obtain

$$u_1 = x_1/\tau = k_1 (1 - x_1) C_{\text{meth}}$$

where $k_1 = x_1/(1 - x_1)\,\tau$. For reaction (2) we have

$$u_2 = C_{\text{CO}}/\tau = C_{\text{meth}} (x_1 - x_2)/\tau = k_2 C_{\text{meth}} x_2$$

where $k_2 = (x_1 - x_2)/x_2\tau$. The time of contact between the gas and the catalyst is $\tau = v_{\text{cat}}/V_g = 5/10\,000 = 5 \times 10^{-4}$ h. Hence, we obtain $k_1 = 0.98/(1 - 0.98) \times 5 \times 10^{-4} = 0.98 \times 10^5\ \text{h}^{-1}$ and $k_2 = (0.98 - 0.9)/0.9 \times 5 \times 10^{-4} = 1.78 \times 10^2\ \text{h}^{-1}$. Since $k_1/k_2 = 5.5 \times 10^2$ we can see that the rate of the main reaction (1) owing to selective catalysis is much higher than the rate of the side reaction (2).

Problem 4. Using the results discussed in Problem 3 determine the parameters of a fluidized-bed reactor producing 15 000 tons of 37% formalin a year. Calculate the reactor diameter D, the catalyst volume, and the height of the catalyst bed (at rest) if the gas velocity is $w_g = 0.6$ m/s.

Solution. Formalin is the aqueous solution of formaldehyde. The reactor should produce 1900 kg/h of formalin, that is, $1900 \times 0.37 = 703$ kg/h of formaldehyde. The consumption of methanol for production of formaldehyde is $703 \times 32/30x_2 = 703 \times 32/30 \times 0.9 = 834$ kg/h $= 834 \times 22.4/32 = 584\ \text{m}^3/\text{h}$. The consumption of the starting gas mixture is $V_g = 584/0.065 = 8960\ \text{m}^3/\text{h}$. Since $V_g = wS \times 3600 = 0.6 \times 0.785D^2 \times 3600$ we find the reactor diameter $D = 2.3$ m. The cross-section area of the reactor is $S = 4.15\ \text{m}^2$. The time of contact between the catalyst and the gas is taken from Problem 3—$\tau = 5 \times 10^{-4}$ h. Hence we can find the catalyst volume—$v_{\text{cat}} = V_g\tau = 8960 \times 5 \times 10^{-4} = 4.48\ \text{m}^3$ and the height of the catalyst bed—$H = v_{\text{cat}}/S = 4.48/4.15 = 1.08$ m.

Problem 5. For the process described in Problems 3 and 4 find approximately the catalyst volume in the fluidized-bed reactor with three beds. The degree of conversion $x_1 = 0.98$.

Solution. As shown in Introduction to Chapter V, when we increase the number of stages in the cascade of complete-mixing reactors (or the number of beds in the fluidized-bed reactor) the distribution of the residence times tends to the distribution of the residence times in the ideal plug-flow reactor. Therefore, we shall tentatively

estimate the time of contact between the gas and the catalyst in the three-bed reactor using the kinetic equations for the plug-flow reactor.

The kinetic equation for the first-order reaction is given by Eq. (IV.22a):

$$dx/d\tau = k_1 (1 - x) \quad \text{or} \quad dx/(1 - x) = k_1 \, d\tau.$$

Hence the time of contact is

$$\tau = \frac{1}{k_1} \int_0^{0.98} dx/(1-x) = \frac{1}{k_1} [\ln (1-0.98) - \ln (1-0)] = 3.98 \times 10^{-5} \text{ h}$$

The reaction rate constant for oxidation of methanol is $k_1 = 0.98 \times 10^5$ h^{-1} (see Problem 3). The catalyst volume is $v_{cat} = V_g \tau = 8960 \times 3.98 \times 10^{-5} = 0.357$ m^3. This volume is smaller by a factor of 12.5 than the catalyst volume in the single-bed reactor of the same productivity.

Thus, the increase in the number of beds in the fluidized-bed reactor results in a sharp decrease in the time of contact between the gas and the catalyst and a decrease in the catalyst volume. However, a reactor with a larger number of beds is more complicated and expensive and its maintenance costs are higher. The optimum number of beds in the reactor is found by means of costs-benefits analysis.

Problem 6. A first-order exothermic reaction occurs in the filter bed of catalyst. The initial temperature in the bed is $t_i = 300$ °C. In the course of the adiabatic process the temperature in the bed increased up to t_f. Then the reaction is carried out in the fluidized-bed reactor under the conditions close to complete mixing. The degree of conversion is $x = 0.35$. The activation energy of the catalytic reaction is $E = 20\,000$ kJ/kmole. The heat of the reaction is $q = 22\,800$ kJ/kmole. The mean specific heat of the reaction mixture is $c = 19$ kJ/kmole K. The concentration of the product in the final reaction mixture is $C = 5.2 \times 10^{-3}$ kmole/m^3. Find the ratio between the reaction rate constants in the fluidized-bed isothermal reaction and the filter-bed adiabatic process.

Solution. The final temperature in the filter-bed reactor is given by Eq. (VI.36):

$$t_f = t_i + qCx/c = 300 + 22\,800 \times 0.25 \times 0.35/19 = 405 \text{ °C}$$

The product concentration (in molar fractions) is

$$C' = CRT/P = 5.2 \times 10^{-3} \times 8.3 \times 10^3 \times 573/9.81 \times 10^4 = 0.25$$

The increase of the temperature in the isothermal fluidized-bed reactor compared with the adiabatic reactor can be estimated with the factor $m = t_f \times 2.3 \log (t_f/t_i)/(t_f - t_i) = 405 \times 2.3 \log (405/300)/105 = 1.15$.

The ratio between the reaction rate constants in the isothermal reactor (k_1) and the adiabatic reactor (k_2) can be found from Eq. (IV.27)

with k_0 = const: $k_1 = k_0 \exp(-20\,000/8.3 \times 678) = k_0 \exp(-3.55)$, $k_2 = k_0 \exp(-20\,000 \times 1.15/8.3 \times 678) = k_0 \exp(-4.1)$, $\log(k_1/k_2) = 0.434\,(4.1 - 3.55) = 0.239$. Hence we obtain

$$k_1/k_2 = 1.75$$

that is, under the same reaction conditions the reaction rate constant in the fluidized bed is higher than that in the filter bed by a factor of 1.75.

The ratio k_1/k_2 increases with increasing degree of conversion. For instance, for $x = 0.75$ and $t_f = 530$ °C we have $m = 530 \times 2.3 \log(530/300)/230 = 1.3$, $k_1 = k_0 \exp(-20\,000/8.3 \times 803) = k_0 \exp(-3.0)$, $k_2 = k_0 \exp(-20\,000 \times 1.3/8.3 \times 803) = k_0 \exp(-3.9)$, $\log(k_1/k_2) = 0.39$, and $k_1/k_2 = 2.5$.

Problem 7. The reaction of NO oxidation is catalyzed by activated and promoted charcoal. The rate of this catalytic equation (in kmoles of converted NO per 1 kg of catalyst per 1 hour) is given by the empirical equation

$$u = p_{NO}^2 p_{O_2}/(a + bp_{NO}^2 + cp_{NO_2}^2)$$

where $a = 16.19$, $b = 4.842 \times 10^5$, and $c = 135$.

The bulk density of the catalyst is $G_{cat} = 480$ kg/m³, $P = 3 \times 10^5$ Pa. The starting gas mixture contains air and 1.5 mol. % of NO. The degree of conversion is $x = 90\%$. Find the volume of the reactor producing 50 tons of NO_2 per day.

Solution. Let us calculate the partial pressures of the components of the final reaction mixture. The productivity of the reactor is $50\,000/24 \times 46 = 45.3$ kmole/h of NO_2. The respective amount of NO ($x = 0.9$) is $45.3/0.9 = 50.3$ kmole/h. The flow rate of the starting gas mixture is $50.3 \times 30/0.015 = 100\,500$ kg/h. Calculations give the following composition of the final reaction mixture:

	NO	O_2	NO_2
N (mol. fractions)	0.014	0.204	0.0129
$p = NP$ (Pa)	4.2×10^3	6.12×10^4	3.8×10^3

Hence, the reaction rate is $u = 0.126$ kmole of NO per 1 kg of catalyst per 1 hour.

If the filling factor $\sigma = v_{cat}/v_r = 1$, that is, the volume of the reactor equals the volume of the catalyst we have $v_r = v_{cat} = G_{NO}/uG_{cat}$ where G_{NO} is the consumption of (converted) NO in kmole/h. We obtain $v_r = 50.3/0.126 \times 480 = 0.83$ m³. If $\sigma < 1$ we have $v_r = v_{cat}/\sigma$.

Problem 8 (modified from [5]). The catalytic gas reaction $A \rightarrow 4R$ occurs at the pressure 3.1×10^5 Pa and the temperature 117 °C in the laboratory reactor with ideal plug flow. The volume of the catalyst is 10 cm³. The starting mixture containing the component A

and the product R flows through the reactor with the rate 20 litres/h. The following experimental results have been obtained.

Concentration of A (mole/litre)	Experiment number 1	2	3	4
C_{A_i}	0.100	0.080	0.060	0.040
C_{A_f}	0.084	0.070	0.055	0.038

Write down the kinetic equation for this reaction and using the equation find the volume of the reactor which is needed for the degree of conversion of 0.35 if the flow rate of the reactant A is 2000 mole/h.

Solution. The largest deviation from the mean concentration is 8% (experiment 1). Hence, we can assume that the reaction rate in this reactor is practically constant throughout the volume of the reactor since variation of the concentration in the reactor is small.

Eq. (V.14) yields for the ideal plug-flow reactor

$$v/G_i = \int_{x_i}^{x_f} dx/u = \frac{1}{-u_m} \int_{x_i}^{x_f} dx = \frac{x_{A_f} - x_{A_i}}{-u_m} \qquad \text{(VI.47)}$$

or

$$-u_m = \frac{G_i (x_f - x_i)}{v_m} \qquad \text{(VI.47a)}$$

The kinetic studies are carried out according to the following procedure: (1) A number of experiments are carried out in the reactor with various initial concentrations of the reactants. (2) The values of C_{A_i}, X_{A_i}, X_{A_f}, G_i, and v are found for each experiment. (3) The value of u_m is found for each experiment from the kinetic equation.

(a) To find the degree of conversion of A we have first to find the initial concentration of A: $C_{A_i} = N_{A_i}/v = P/RT = 3.1 \times 10^5/8.3 \times \times 10^3 \times 390 = 0.1$ mole of A per 1 litre of the gas mixture. The rate of feeding of A is $G_i = C_{A_i} v = 0.1 \times 20 = 2$ mole/h.

In the reaction with variation of volume the concentration of the starting component and the degree of conversion are related by the following equations:

$$\frac{C_A}{C_{A_i}} = \frac{1 - x_A}{1 + \beta_A x_A} \quad \text{or} \quad x_A = \frac{1 - C_A/C_{A_i}}{1 + \beta_A C_A/C_{A_i}} \qquad \text{(VI.48)}$$

Here $\beta_A = 3$ (see Eq. (V.8)).

The results calculated with Eqs. (VI.47a) and (VI.48) are summarized in Table 33.

TABLE 33

C_{A_i}/C_A	C_{A_f}/C_A	C_{A_m} (mole/litre)	$x_{A_i} = \frac{1-C_{A_i}/C_A}{1+\beta C_{A_i}/C_A}$	$x_{A_f} = \frac{1-C_{A_i}x/C_A}{1+\beta C_{A_i}x/C_A}$	$\Delta x_A = x_{A_i} - x_{A_f}$	$u = \frac{\Delta x_A}{v/C_A}$	$1/u$	x_{A_m}
1	0.84	0.092	$\frac{1-1}{1+3}=0$	$\frac{1-0.84}{1+3\times0.84}=0.0455$	0.0455	9.1	0.11	0.02275
0.8	0.70	0.075	0.0588	0.0968	0.0380	7.6	0.1316	0.0778
0.6	0.55	0.0575	0.1429	0.1698	0.0269	5.4	0.186	0.1563
0.4	0.38	0.039	0.2727	0.2897	0.0170	3.4	0.294	0.2812

These data can be used to plot u_A as a function of C_A (see Fig. 18). The plot is a straight line passing through the origin. This indicates that catalytic decomposition of A is a first-order reaction. The slope

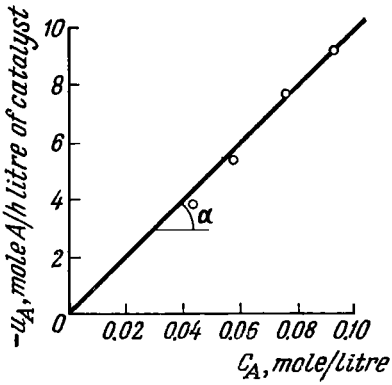


Fig. 18. Determination of the driving force and the rate constant of the catalytic reaction in Problem 8.

of the plot in Fig. 18 yields the reaction rate constant $k = 96$ litres of the gas per 1 hour per 1 litre of the catalyst.

Now the kinetic equation for the reaction can be written as

$$-u_A = \frac{1}{v}\frac{dN_A}{d\tau} = 96C_A$$

(b) The catalyst volume v_{cat} needed for reaching the given degree of conversion x is given by the kinetic equation for the ideal plug-

flow reactor (V.14):

$$v_{cat} = G_1 \int_0^{x_A} dx_A / kC_1 = \frac{G_1}{kC_1} \int_0^{x_A} \frac{1+\beta_A x_A}{1-x_A} dx_A$$

$$v_{cat} = \frac{G_1}{kC_1} \left[(1+\beta_A) \ln \frac{1}{1-x_A} - \beta_A x_A \right] \qquad \text{(VI.49)}$$

Eq. (VI.49) yields

$$v_{cat} = \frac{\text{2000 moles of A per 1 hour}}{\left(96 \frac{\text{litre of gas}}{\text{h} \cdot \text{litre of catalyst}}\right)\left(0.1 \frac{\text{mole of A}}{\text{litre of gas}}\right)} \times$$

$$\times (4 \ln (1/0.65 - 0.5)) = 140 \text{ litres}$$

Problem 9. The catalytic reaction $2A \rightarrow R + S$ is carried out in an experimental tubular reactor with a solid catalyst. The reactor operates under the conditions of ideal plug flow. The catalyst volume is 0.1 m³. The flow rate of the gaseous component A is $V_g = 15$ m³/h at $P = 20 \times 10^5$ Pa and $t = 300$ °C. The degree of conversion of the component A is $x = 65\%$. The reaction is described by the kinetic equation $-u_A = kC_A^2$.

Using the experimental results find the catalyst volume in a pilot plant with $x = 0.85$. The starting mixture contains 60% A and is fed into the plant with the flow rate of 230 m³/h. The process is carried out at 300 °C and 40×10^5 Pa.

Solution. The reaction rate constant can be found from the results obtained with the experimental reactor. The concentration of A in the starting gas is $C_{A_1} = P/RT = 20 \times 10^5/573 \times 8.31 \times 10^3 = 0.425$ kmole/m³.

The kinetic equation can be written in terms of the degree of conversion:

$$-u_A = dx/d\tau = kC_{A_1}^2 (1-x)^2 \qquad \text{(VI.50)}$$

Integration of Eq. (VI.50) yields

$$-u_A = \int_0^x dx/(1-x)^2 = kC_{A_1}^2 \tau$$

Hence we obtain

$$\frac{1}{1-x} \Bigg|_0^{0.65} = kC_{A_1}^2 \tau \qquad \text{(VI.51)}$$

The time τ (the theoretical time of residence of the reactants in the reactor) can be found since we know the catalyst volume

in the experimental reactor:

$$\tau = v_{cat}/V_g = 0.1/15 = 0.00668 \text{ h}$$

Hence, we can find the rate constant k from Eq. (VI.51):
$k = 0.65/(1 - 0.65)\ 0.00668 \times 0.425^2 = 1.55 \times 10^3$ m³/kmole h.

We can now find the catalyst volume in the pilot plant. The initial concentration of A in the pilot plant is $C_{A_1} = (40 \times 10^5/573 \times \times 8.31 \times 10^3)\ 0.6 = 0.51$ kmole/m³. The time of contact between the gas and the catalyst needed to reach $x = 0.85$ can be found by integrating the kinetic equation $-u_A = dx/d\tau$:

$$\tau = \int_0^x dx/(-u_A) = \int_0^x dx/kC_{A_1}^2 (1-x)^2 =$$

$$= \frac{1}{1.55 \times 10^3 \times 0.51^2} \cdot \frac{1}{1-x} \Bigg|_0^{0.85} = 1.4 \times 10^{-2} \text{ h}$$

Hence, $v_{cat} = \tau V_g = 1.4 \times 10^{-2} \times 230 = 3.25$ m³

Problem 10. The catalytic gas reaction A → R is studied in the tubular reactor containing 2g (1 cm³) of catalyst. The concentration of A in the gas mixture is measured before contact with the catalyst and after the contact (see Table 34)

TABLE 34

P_{A_1} ($10^3 \times$ Pa)	101.13	86.45	79.80	66.50	59.80	53.20	46.55	39.90	26.60	13.30
P_{A_f} ($10^3 \times$ Pa)	100.30	85.90	79.32	66.17	59.58	52.99	46.39	39.77	26.54	13.28

The gas flow rate is $V_g = 0.01$ litre/s at the pressure $P = 1.013 \times \times 10^5$ Pa and the temperature $t = 450$ °C.

Write down the kinetic equation for the reaction in gas concentration units per unit bulk volume of the catalyst. Find the volume of the ideal plug-flow reactor providing for the degree of conversion $x = 50\%$ if the gas flow rate is $V_g = 20$ kmoles of A per 1 hour.

Solution. Since the degree of conversion of A in one cycle is small we can use the differential technique for analysing the reaction kinetics. The consumption of component A (in moles/h) is

$$V_{A_1} = (p_{A_1} V_g \times 3600/101.3 \times 22.4) \times (273/96.2) = 4.5 \times 10^{-2} p_{A_1}$$

where 96.2 is the factor for reduction to normal conditions and suitable dimensions.

The concentration of A in the starting mixture (in moles/litre) is

$$C_A = V_{A_1}/V_g \times 3600 = V_{A_1}/36$$

To calculate the consumption V_A in the conventional units (to find the contact time τ in the time units rather than the arbitrary units) the parameters V_{A_i}, C_A, and u_A should be multiplied by $22.4 \times 96.2/273 = 7.85$ litre/mole, that is by the volume of 1 mole of A under the process conditions. Then we obtain

$$V_{A_i}\ \text{(litre/h)} = V_{A_i}\ \text{(mole/h)} \times 7.85\ \text{(litre/mole)}$$

$$u_A = xV_{A_i}\ \text{(litre/h)} = u_A\ \text{(mole/h)} \times 7.85\ \text{(litre/mole)}$$

$$u'_A = xV_{A_i}/v_{cat}\ \text{(litre/h litre of catalyst)} =$$

$$= u'_A\ \text{(mole/h litre of catalyst)} \times 7.85\ \text{(litre/mole)}$$

$$C_{A_i}\ \text{(litre of A/litre)} = C_{A_i}\ \text{(mole/litre)} \times 7.85\ \text{(litre/mole)}$$

Table 35 presents the results obtained from the experimental data of Table 34.

TABLE 35

P_{A_i} (10^3 Pa)	P_{A_f} (10^3 Pa)	$x = \frac{P_{A_i} - P_{A_f}}{P_{A_i}} \times 10^3$	V_{A_i} (litre/h)$\times 10^3$	$-u_A = xV_{A_i}$ (litre/h)$\times 10^3$	$-u'_A = xV_{A_i}/v_{cat}$ (litre of A/h litre of catalyst)	C_A (litre of A/litre)	C_A^2 (litre^2 of A/litre^2)
101.10	100.30	7.63	36.1	275	275	1.00	1.00
86.45	85.90	6.45	30.4	200	200	0.86	0.745
79.80	79.32	6.00	28.5	171	171	0.79	0.63
66.50	66.17	5.00	23.8	119	119	0.66	0.44
59.80	59.58	4.45	21.4	95	95	0.594	0.35
53.20	52.99	4.00	19.0	76	76	0.53	0.28
46.55	46.39	3.43	16.6	57	57	0.46	0.22
39.90	39.77	3.00	14.3	42.8	42.8	0.395	0.156
26.60	26.54	2.00	9.5	19.0	19.0	0.264	0.07
13.30	13.28	1.00	4.75	4.75	4.75	0.132	0.017

Let us assume that u_A is proportional to C_A. The function $-u_A = f(C_A^2)$ plotted from the data of Table 35 is not a straight line so that the assumption is not correct.

The plot u_A *vs.* C_A^2 (see Fig. 19) is a straight line passing through the origin. Hence the kinetic equation for the reaction can be written as

$$-u_A = kC_A^2$$

Let us find the reaction rate constant: $k = -u'_A/C_A^2 = 275/1.02 = 274$ litre²/h litre of catalyst litre of A.

In a similar way for the reaction rate u_A (in litre/h) we obtain $k = 0.275/1.02 = 0.274$ litre²/h litre. The respective kinetic equation (in litre/h) is $-u_A = 0.274\, C_A^2$ and the kinetic equation (in litre/h litre of catalyst) is $-u'_A = 274 C_A^2$.

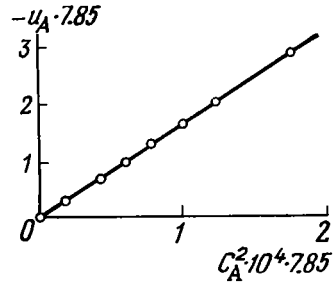


Fig. 19. Determination of the driving force of the catalytic reaction in Problem 10.

The above results make it possible to find the catalyst volume of the industrial reactor with $x = 50\%$. For the ideal plug-flow reactor we have $-u_A = dx/d\tau$. Since $\tau = v_{cat}/V_{A_i}$ and $d\tau = dv_{cat}/dV_{A_i}$ we obtain $-u'_A = V_{A_i}\, dx/dv_{cat}$ so that $dv_{cat} = V_{A_i}\, dx/(-u'_A)$. Since we have $-u'_A = 274 C_A^2$ and $C_A = C_{A_i}(1 - x)$ we obtain

$$v_{cat} = \int_0^x dx V_{A_i}/274 C_{A_i}^2 (1-x)^2 = (V_{A_i}/274 C_{A_i}^2) \int_0^x dx/(1-x)^2 =$$

$$= 20\,000 \times 59.4/274 \times 1.00^2)\,(0.5/0.5) =$$

$$= 4300 \text{ litres or } 4.3 \text{ m}^3$$

Problem 11 (modified from [22]). The contact process of catalytic oxidation of ammonia proceeds in the reactor under the pressure $P = 1 \times 10^5$ Pa. The starting gas contains 10% (by volume) NH_3 and 90% air. The degree of conversion of NH_3 into NO is 0.95. The starting temperature is 20 °C; the reaction temperature is 700 °C (that is lower than the typically used temperature). The productivity of the reactor is 600 kg of NH_3 per day per 1 m² of the catalyst surface. The mass flow rate of the gas is $G = 573.6$ kg/m² h. The diameter of the platinum wire of the gauze is 0.06 mm. Find the height of the catalyst layer (the packets of the platinum wire gauze).

Solution. Oxidation of ammonia can involve the following reactions:

$$4NH_3+5O_2=4NO+6H_2O \quad (1)$$

$$4NH_3+4O_2=2N_2O+6H_2O \quad (2)$$

$$4NH_3+3O_2=2N_2+6H_2O \quad (3)$$

All these reactions are practically irreversible and the yield of the main product, NO, that is the reaction selectivity, is determined by the ratio of the rates of the reactions (1)-(3). In the presence of a fine selective platinum catalyst reaction (1) is sharply accelerated (this process is used as the first stage in production of nitric acid). In the optimum temperature range from 850 to 900 °C where the rates of the side reactions are slow (with the platinum catalyst) the degree of oxidation of ammonia to NO is 95-98% for a rather small time of contact between the gas and the catalyst (10^{-4} s). The process is limited by external diffusion.

To find the diffusion coefficients we should determine the composition of the final gas mixture from the material balance. Since the reactions (2) and (3) yield only small amounts of N_2 and N_2O we can ignore them. The amount of oxidized ammonia per 1 m^2 of the catalyst surface is $600 \times 1.41/24 = 35.1$ kg/h. Table 36 presents the material balance of the process per 1 m^2 of the platinum gauze per 1 hour.

TABLE 36

Inputs					Outputs				
Material	kmoles	m^3	kg	% by volume	Product	kmoles	m^3	kg	% by volume
NH_3	2.07	46.2	35.1	10.0	NO	1.97	44.0	58.6	9.22
O_2	3.94	88.1	126.0	17.9	H_2O	3.1	69.5	56.0	14.64
N_2	14.76	330.0	412.5	72.1	O_2	1.4	31.4	45.0	6.57
					N_2	14.81	332.0	414.0	69.57

To determine the height of the catalyst layer we can use the above procedure for calculating the rate of a catalytic process limited by mass transfer from the height of transfer unit (HTU) and the number of transfer units (Z) (see Eqs. (VI.16)-(VI.20)). First we should determine the densities ρ, viscosities μ, and the diffusion coefficients D of the starting and final gas mixture (see Table 37).

The mean molecular mass of the starting mixture (at 20 °C) is 27.6 and the mean density is 1.156. The mean molecular mass of the final mixture (at 700 °C) is 27.0 and the mean density is 0.339.

TABLE 37

t (°C) Parameter	Gas components				
	NH_3	O_2	N_2	H_2O	NO
20 ρ (kg/m³)	0.71	1.33	1.16	—	—
μ (kg/m h)	0.034	0.075	0.064	—	—
ρ (kg/m³)	—	0.40	0.35	0.23	0.38
700 μ (kg/m h)	0.116	0.174	0.144	0.15	0.154

The diffusion coefficients can be found from the following general relationships. For diffusion of the gas A in the gas B we have

$$D_{AB} = 0.0043 \frac{T^{3/2}}{P\left(v_A^{1/3} + v_B^{1/3}\right)^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \qquad \text{(VI.52)}$$

where v_A and v_B are the molar volumes of the gases A and B (m³/mole). The molar volumes can be taken from the handbooks: NH_3—25.8, O_2—25.6, N_2—31.2, NO—23.6, H_2O—18.9.

The diffusion coefficient for the gas A in the gas mixture is given by the following equation:

$$D_{A_m} = \frac{1 - N_A}{\frac{N_B}{D_{AB}} + \frac{N_C}{D_{AC}}} \qquad \text{(VI.53)}$$

Here N_A, N_B, N_C are the molar fractions of the components in the gas mixture and D_{AB}, D_{AC} are the diffusion coefficients for the binary gas mixtures given by Eq. (VI.52).

The table below presents the calculated diffusion coefficients of ammonia and other components of the starting and final gas mixtures in the binary mixtures and the diffusion coefficients D_{NH_3} of ammonia in the starting and final reaction mixtures (in m²/h):

0.067	0.064	0.054	0.065	20 °C
D_{NH_3, O_2}	D_{NH_3, N_2}	D_{O_2, N_2}	$D_{NH_3 \to O_2, N_2}$	
0.407	0.392	0.329	0.582	
D_{NH_3, O_2}	D_{NH_3, N_2}	D_{O_2, N_2}	D_{NH_3, H_2O}	
0.422	0.364	0.504	0.464	700 °C
$D_{NH_3, NO}$	$D_{O_2, NO}$	D_{O_2, H_2O}	D_{NO, H_2O}	
0.345	0.427	—	0.412	
D_{NO, N_2}	D_{N_2, H_2O}		$D_{NH_3 \to (O_2, N_2, NO, H_2O)}$	

The mean viscosity of the gas mixture is found from the following equation:

$$\mu_m = \frac{\mu_1}{1+\frac{1.38}{N_1\rho_1}\left(\frac{N_2}{D_{1,2}}+\frac{N_3}{D_{1,3}}+\ldots\right)} + \frac{\mu_2}{1+\frac{1.38}{N_2\rho_2}\left(\frac{N_1}{D_{2,1}}+\frac{N_3}{D_{2,3}}+\ldots\right)}$$

Here N_1, N_2, and N_3 are the molar fractions of the components of the gas mixture. The mean viscosity of the gas mixture is $5.7 \times \times 10^{-2}$ Pa h at 20 °C and 1.15×10^{-1} Pa h at 700 °C.

To calculate the HTU and Z values we assume that the platinum gauze layer is similar to the Raschig ring packing with $d = h = 0.06$ mm (equal to the wire diameter). The equivalent diameter for such rings is $d_e = \sqrt{1.5}\, d = 7.3 \times 10^{-5}$ m. The specific surface of the rings is $S_{sp} = 2.84 \times 10^4$ m²/m³.

To find the HTU value from Eq. (VI.19) we have to calculate the Reynolds number $Re = G_g d_e/\mu_m$ and the diffusion Prandtl criterion $Pr' = \mu_m/\rho_m D_{NH_3}$. For the conditions of this problem we obtain $Re_{20} = 0.73$, $Re_{700} = 0.367$, $Pr'_{20} = 0.76$ and $Pr'_{700} = 0.812$. The mass-transfer coefficient is

$$k_M = 1.82 Re^{-0.51} \qquad (VI.54)$$

Hence, we can write Eq. (VI.19) as

$$HTU \cdot S_{sp} = (Pr')^{2/3}/k_M$$

For the starting reaction mixture at 20 °C we have $k_M = 2.14$ and $HTU \cdot S_{sp} = 0.39$; for the final mixture at 700 °C we have $k_M = 3.04$ and $HTU \cdot S_{sp} = 0.287$. Then we obtain

$$HTU = \frac{\frac{0.39+0.287}{2}}{2.84\times10^4} = 1.2 \times 10^{-5} \text{ m}$$

Eq. (VI.20) yields the following approximate equation for the number Z of the transfer units

$$Z = C_{m.\,log} \ln \frac{C^i_{NH_3}(1+\beta^f_{NH_3})}{C^f_{NH_3}(1+\beta^i_{NH_3})} \qquad (VI.55)$$

where β is the variation of the number of moles owing to the reaction per 1 mole of NH_3, $C^i_{NH_3}$ and $C^f_{NH_3}$ are the concentrations of NH_3 in the initial and final reaction mixtures (molar fractions) and

$$C_{m.\,log} = \frac{(1+C_{NH_3}\beta)-(1+C^{cat}_{NH_3}\beta)}{\ln\frac{1+C_{NH_3}\beta}{1+C^{cat}_{NH_3}\beta}}$$

where $C^{cat}_{NH_3}$ is the ammonia concentration at the catalyst surface (in molar fractions).

For oxidation of ammonia over the platinum catalyst we can assume $C_{NH_3}^{cat} = 0$ since the rate of the reaction at the catalyst surface is very high. Then we have $C_{m.log} = 1$. The molar fraction of ammonia in the final reaction mixture is $C_{NH_3}^{f} = 0.002$. Hence, we obtain $Z = 1 \times 2.3 \log (0.1 (1 + 0.2 \times 0.25)/0.002 (1 + 0.1 \times \times 0.25)) = 3.94 \approx 4$. The height of the catalyst layer is $H_{cat} = = Z \cdot HTU = 1.2 \times 10^5 \times 4 = 4.8 \times 10^{-5}$ m $= 0.048$ mm.

Since the surface of the catalyst rings available for the reaction is approximately twice that of the wire gauze we have to multiply the result by a factor of 2 and obtain $H_{cat} = 2 \times 0.048 = 0.096$ mm. This means that two platinum gauzes are needed. As the upper gauze rapidly burns out owing to platinum removal three gauzes are typically installed.

Problem 12. Find the hydraulic resistance of the filter catalyst bed with the height $H = 1.7$ m in the reactor with the diameter $D = 2.5$ m. The gas flow rate is $V_g = 8500$ m^3/h, the gas density is $\rho_g = 0.45$ kg/m^3, and the gas viscosity is $\mu = 0.294 \times 10^{-4}$ Pa s. The specific surface area of the catalyst particles is $S = 415$ m^2/m^3, the porosity of the catalyst bed is $\varepsilon = 0.43$. The number of catalyst particles in 1 m^3 of the bed was found to be $m = 10^6$. Find the shape factor Φ and the equivalent diameter d_e of the pore in the catalyst bed.

Solution. The cross-section area of the reactor is $F = 4.9$ m^2. The theoretical gas velocity is $w_{th} = V_g/3600 \times 4.9 = 0.482$ m/s. The Reynolds number is

$$\mathrm{Re} = w d_e \rho/\mu = 4 w_{th} \rho/S\mu \qquad \text{(VI.56)}$$

where d_e is the mean equivalent diameter of the pore in the catalyst bed ($d_e = 4\varepsilon/S$ and $w = w_{th}/\varepsilon$). Hence, we obtain $\mathrm{Re} = 4 \times \times 0.482 \times 0.45/415 \times 0.294 \times 10^{-4} = 71$. The resistance coefficient is $\xi = 11.6/71^{0.25} = 4$. According to Eq. (VI.41) the hydraulic resistance of the catalyst bed is

$$\Delta p = \xi H S \rho w_{th}^2/8\varepsilon^3 = 4500 \text{ Pa}$$

The equivalent pore diameter is

$$d_e = 4\varepsilon/S = 4 \times 0.43/415 = 0.414 \times 10^{-2} \text{ m}$$

The shape factor for the particles is

$$\Phi = S_s/S_p$$

where S_p is the surface area of the catalyst particle and S_s is the surface area of the sphere with the same volume. The particle volume is

$$v_p = (1 - \varepsilon)/m = \pi d^3/6 \qquad \text{(VI.57)}$$

and the particle surface area is

$$S_p = S/m = \pi d^2/\Phi \qquad \text{(VI.58)}$$

Here d is the diameter of the sphere with the same volume as that of the catalyst particle, (m).

Hence we obtain

$$S = 6\,(1 - \varepsilon)/\Phi d \qquad \text{(VI.59)}$$

The diameter d can be found from Eq. (VI.57):

$$d = \sqrt[3]{6\,(1 - \varepsilon)/\pi m} = \sqrt[3]{6\,(1 - 0.43)/3.14 \times 10^6} = 0.0103 \text{ m}.$$

The shape factor can be derived from Eq. (VI.59):

$$\Phi = 6\,(1 - \varepsilon)/Sd = 6\,(1 - 0.43)/415 \times 0.0103 = 0.8$$

Problem 13. A reaction is carried out in the fluidized bed in the reactor with the diameter $D = 152$ mm and the height $H = 305$ mm. The volume rate of flow of the gas is $V_v = 125$ m^3/h per 1 m^3 of catalyst. The density of catalyst is $\rho_{cat} = 4400$ kg/m^3, the shape factor of the catalyst particles is $\Phi = 0.58$. The gas viscosity is $\mu = 1.8 \times 10^{-3}$ Pa s, the gas density is $\rho_g = 1.2$ kg/m^3. The kinetic studies have shown that the hydraulic resistance of the fluidized bed should not exceed $\Delta P = 7000$ Pa. Find the minimum size of the catalyst particles.

Solution. The hydraulic resistance of the fluidized bed should be constant; it can be found from Eq. (VI.42):

$$\Delta P = \rho_{cat} g\,(1 - \varepsilon)\,H_b$$

Let us assume that the height of the bed H_b is equal to the height H of the reactor. The porosity of the catalyst bed for the maximum permissible ΔP can be found from Eq. (VI.42):

$$\varepsilon = 1 - \Delta P/\rho_{cat} g H = 1 - 7000/4400 \times 9.8 \times 0.305 = 0.465$$

The porosity of the bed can also be found from the equation

$$\varepsilon = (v_b - v_{cat})/v_b$$

where v_b is the volume of the bed and v_{cat} is the volume of the catalyst. Thus, we have $v_{cat} = v_b\,(1 - \varepsilon) = \pi D^2 H\,(1 - \varepsilon)/4 = 3.14 \times 0.152^2 \times 0.305 \times (1 - 0.465)/4 = 0.003$ m^3.

The linear velocity of the gas in the reactor is

$$w = V_g/S = V_v v_{cat}/S = 4V_v v_{cat}/\pi D^2 = 125 \times 0.003 \times 4/3600 \times 3.14 \times 0.152^2 = 0.00573 \text{ m/s}$$

The condition for removal of the catalyst particles is given by Eq. (VI.33):

$$Re_{rem} = Ar_{min}/(18 + 0.6\sqrt{Ar_{min}})$$

We have

$$\mathrm{Re_{rem}} = w\, d\rho_g/\mu_g = 0.00573 \times 1.2 \times d/1.8 \times 10^{-3} = 3.83d$$

and

$$\mathrm{Ar_{min}} = d^3 (\rho_{cat} - \rho_g)\, \rho_g g/\mu^2 = \\ = 4400 \times 1.2 \times 9.8/1.8^2 \times 10^{-6} = 1.6 \times 10^{10} d^3$$

Thus, $3.83d = 1.6 \times 10^{10}\, d^3/(18 + 0.6 \sqrt{1.6 \times 10^{10}\, d^3})$. Hence, we find (by trial-and-error technique) $d = 6.57 \times 10^{-5}$. Using the shape factor we find the particle diameter

$$d_p = \Phi d = 0.58 \times 6.57 \times 10^{-5} = 3.79 \times 10^{-5} \text{ m} \approx 0.04 \text{ mm}$$

Problem 14. A catalytic reaction is studied in a laboratory reactor with the fluidized bed of the (nickel) Fischer-Tropsch catalyst. The reactor diameter is $D = 0.61$ m; the volume of the catalyst bed at rest is $v = 0.093$ m^3; the mass rate of flow of the gas is $G_g = 7.0$ kg/m^2 h; the density of the catalyst particles is $\rho_{cat} = 5000$ kg/m^3; the shape factor of the particles is $\Phi = 0.58$; the gas viscosity is $\mu = 0.256 \times 10^{-3}$ Pa s; the density of the initial gas is $\rho_g^i = 14.45$ kg/m^3 and the density of the final gas products is $\rho_g^f = 16.52$ kg/m^3.

Find the maximum diameter of the particles in the fluidized bed and the degree of expansion of the bed for the mean diameter $d_m = 0.6\, d_{max}$.

Solution. Assuming that the conditions in the catalyst bed are close to complete mixing we shall calculate the gas velocity for the gas density equal to the final gas density:

$$w = G_g/3600\rho_g^f = 7.0/3600 \times 16.5 = 0.117 \times 10^{-3} \text{ m/s}$$

The critical velocity for suspension of the uniform bed of spherical particles is given by Eq. (VI.29):

$$\mathrm{Re_{susp}} = \mathrm{Ar}/(1400 + 5.22 \sqrt{\mathrm{Ar}})$$

where $\mathrm{Re_{susp}} = w_{susp}\, d\rho_g/\mu$ and $\mathrm{Ar} = gd^3 (\rho_{cat} - \rho_g)\, \rho_g/\mu^2$. We assume $w = w_{susp}$ and $d = d_{max}$. Then we have $\mathrm{Re_{susp}} = (0.117 \times 10^{-3} \times 16.52/0.256 \times 10^{-3})\, d_{max} = 7.6\, d_{max}$, $\mathrm{Ar} = (1500 - 16.52)\, 16.52 \times 9.8\, d_{max}^3/(0.256 \times 10^{-3})^2 = 12.3 \times 10^{12} d_{max}^3$ and $7.6 d_{max} = 12.3 \times 10^{12} d_{max}^3/(1400 + 5.22 \sqrt{12.3 \times 10^{12} d_{max}^3})$. Hence we find (by trial-and-error technique) $d_{max} = 2.94 \times 10^{-5}$ m. Taking into account the shape factor we obtain

$$d'_{max} = \Phi d_{max} = 0.58 \times 2.94 \times 10^{-5} = 1.7 \times 10^{-5} \text{ m}$$

The mean diameter of the particles is

$$d_m = 0.6 d_{max} = 0.6 \times 2.94 \times 10^{-5} = 1.71 \times 10^{-5} \text{ m}$$

For the particles with the mean diameter d_m we have

$$Ar_m = (\rho_{cat} - \rho_g)\,\rho_g g d_m^3/\mu^2 = 12.3 \times 10^{12} \times 1.71^3 \times 10^{-15} = 6.14 \times 10^{-2}$$

For the critical rate of suspension of the particles with d_m we have $Re_{m.\,susp} = Ar_m/(1400 + 5.22\sqrt{Ar_m}) = 4.38 \times 10^{-5}$.

The porosity of the fluidized bed with d_m can be found from Eq. (VI.44): $\varepsilon_0 = ((18Re_{m.\,susp} + 0.36Re^2_{m.\,susp})/Ar_m)^{0.21} = 0.398$. The porosity of the fluidized bed for the gas velocity $w = 0.117 \times \times 10^{-3}$ m/s is $\varepsilon = ((18Re_m + 0.36Re_m^2)/Ar_m)^{0.21}$ where $Re_m = = 0.117 \times 10^{-3} \times 1.71 \times 10^{-5} \times 16.52/0.256 \times 10^{-3} = 1.29 \times 10^{-4}$. Hence, $\varepsilon = ((18 \times 1.29 \times 10^{-4} + 0.36 \times 1.29^2 \times 10^{-8})/6.14 \times \times 10^{-2})^{0.21} = 0.502$.

The initial height of the catalyst bed is

$$H_0 = 4v_b/\pi D^2 = 4 \times 0.0943/3.14 \times 0.61^2 = 0.322 \text{ m}$$

The height of the fluidized catalyst bed is given by Eq. (VI.43):

$$H = H_0\,(1 - \varepsilon_0)/(1 - \varepsilon) = 0.39$$

The degree of expansion of the catalyst bed is 1.21.

Problem 15. Formaldehyde is produced by partial oxidation of the natural-gas methane in the reactor with the fluidized bed of silver catalyst (on the aluminosilicate substrate). The initial gas mixture consists of the natural gas containing 97.1% (by volume) of CH_4 and air and has the following composition (in % by volume): CH_4—26.5, O_2—14.8, N_2—58.7. The final gas mixture after removal of the soluble reaction products has the following composition (in % by volume): CH_4—25.8, O_2—11.8, CO_2—0.2, CO—0.4, C_nH_m—0.2, H_2—1.0, N_2—60.5. The volume flow rate of the gas mixture is $V_v = 3000$ m³/h, the temperature in the reaction zone is 750 °C. The process yields 30 g of CH_2O and 3.4 g of CH_3OH per 1 m³ of the natural gas. The diameter of the reactor is 1 m. The spherical particles of catalyst have the mean diameter $d = 1.5$ mm. The density of the catalyst is $\rho_{cat} = 1200$ kg/m³. The density of the gas mixture under the reaction conditions is $\rho_g = 1.215$ kg/m³. The viscosity of the gas mixture under the reaction conditions is $\mu = 1.835 \times 10^{-5}$ Pa s.

Calculate (1) the degree x of conversion of methane into the main products—formaldehyde and methanol; (2) the critical and operational rates of suspension w_{cr} and w; and (3) the productivity Π of the reactor, the catalyst volume v_{cat}, the height H of the catalyst bed and the hydraulic resistance ΔP of the catalyst bed.

Solution. The process of direct oxidation of methane to formaldehyde is carried out with solid catalyst (in particular, with the aluminosilicate catalyst) both in the filter and fluidized beds and in the surface-content apparatus. Each of these technologies have

specific advantages and disadvantages. For instance, the fluidized-bed apparatus decreases the explosion hazard owing to the isothermality of the process and rapid reduction of the concentrations of the components due to mixing.

Homogeneous oxidation of methane involves consecutive chain reactions giving rise to CO_2 and H_2O. The selective solid catalysts sharply increase the rates of the reactions (1), (4), and (6) giving rise to CH_2O and CH_3OH:

$$CH_4 + O_2 \rightarrow CH_2O + H_2O \quad (1)$$

$$CH_2O \rightarrow CO + H_2 \quad (2)$$

$$CH_2O + O_2 = CO_2 + H_2O \quad (3)$$

$$CH_4 + 0.5O_2 = CH_3OH \quad (4)$$

$$CH_4 \rightarrow C + 2H_2 \quad (5)$$

$$CH_3OH + 0.5O_2 = CH_2O + H_2O \quad (6)$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (7)$$

All these reactions, including the main reactions (1), (4), and (6), are practically irreversible. The increase of temperature is limited by acceleration of the undesirable reactions, and the optimum temperature of the process is 750 °C.

The catalytic process gives rise to the gas mixture which contains non-condensing components insoluble in water and the reaction products which are dissolved in water.

(1) Let us find the degree of conversion of methane in the process taking into account the fact that the mass of nitrogen remains constant but its concentration varies: $x_{CH_4} = 100 - 25.8 \times 58.7 \times \times 100/26.5 \times 60.5 = 5.5\%$; $x_{CO_2} = 0.2 \times 58.7 \times 100/26.5 \times \times 60.5 = 0.73\%$; $x_{CO} = 0.4 \times 58.7 \times 100/26.5 \times 60.5 = 1.46$; $x_{C_nH_m} = 0.2 \times 58.7 \times 100/26.5 \times 60.5 = 0.73$. The degrees of conversion of methane into the main products CH_2O and CH_3OH (molecular masses 30 and 32) are $x_{CH_2O} = 30 \times 22.4 \times 100/30 \times \times 1000 \times 0.971 = 2.31\%$ and $x_{CH_3OH} = 3.4 \times 22.4 \times 100/32 \times \times 1000 \times 0.971 = 0.24\%$. Hence, the total degree of conversion of methane is

$$x_{CH_4} = x_{CO_2} + x_{CO} + x_{C_nH_m} + x_{CH_2O} + x_{CH_3OH} = 5.47\%$$

It can be seen that $5.5 - 5.47 = 0.03\%$ of methane is unaccounted for.

The yield of the main products related to the reacted methane is $x = (2.31 + 0.24)/5.5 = 0.464 = 46.4\%$ so that 53.6% of the reacted methane is consumed for production of the side products.

(2) As given by Eq. (VI.29) the critical rate of suspension is

$$w_{susp} = Re_{susp}\mu/d\rho_g$$

where $Re_{susp} = Ar/(1400 + 5.22\sqrt{Ar})$ and $Ar = gd^3(\rho_{cat} - \rho_g)\rho_g/\mu^2 = (1.5 \times 10^{-3})^3 (1200 - 1.215)\, 1.215 \times 9.8/(1.835 \times 10^{-5})^2 = 141\,000$. Hence we obtain $Re_{susp} = 141\,000/(1400 + 5.22\sqrt{141\,000}) = 41.7$ and $w_{susp} = 41.7 \times 1.835 \times 10^{-5}/1.5 \times 10^{-3} \times 1.215 = 0.42$ m/s. The operational velocity of the gas can be taken to be equal to $2.5w_{susp} = 1.05$ m/s.

(3) The gas flow rate per hour is $V_g = wF = w \times 0.785D^2 \times 273/1023 = 0.228$ m³/s = 800 m³/h.

Hence, the flow rate of methane is $v_{CH_4} = 800 \times 0.265 = 212$ m³/h.

The productivity of the reactor is $\Pi = 212 \times 30/0.971 = 6550$ g of CH_2O per hour or $\Pi = 6550 \times 100/30 \times 1000 = 21.8$ litres of 30% formaldehyde solution per hour.

The catalyst volume is $v_{cat} = V_g/V_v = 800 \times 1000/3000 = 266$ litres = 0.266 m³. The height of the catalyst bed at rest is $H_0 = v_{cat}/F = 0.266/0.785 = 0.34$ m.

The hydraulic resistance of the catalyst bed is given by Eq. (VI.42a): $\Delta P = \sigma\rho_b H_0 g = 0.6 \times 1.2 \times 0.34 \times 9.81 \times 10^3 = 2400$ Pa. Here $\sigma = 0.6$ is the factor describing the degree of filling of the apparatus with the catalyst (consisting of spherical particles).

Problem 16. The starting gas mixture flow is fed to the catalytic cracking reactor parallel to the flow of bead catalyst. Calculate the volume v_{int} of the zone of intensive heat exchange after which the temperatures of the flows differ from the heat equilibrium temperatures by 1 K. The flow rate of gas mixture is $G_m = 13.5$ kg/s (48.6 ton/h), the flow rate of catalyst is $G_{cat} = 27$ kg/s (97.2 ton/h), the starting temperature of the gas mixture is $T_m^i = 748$ K and the starting temperature of the catalyst is $T_{cat}^i = 783$ K, the specific heat of the gas mixture is $c_m = 3000$ W s/kg K and that of the catalyst is $c_{cat} = 1000$ W s/kg K, the diameter of the catalyst bead is $d = 3 \times 10^{-3}$ m, the proportion of the free volume in the reaction zone is $\varepsilon = 0.5$; the coefficient of the heat transfer from the catalyst beads to the gas mixture is $\alpha = 465$ W/m² K.

Solution. We can neglect here variations of masses, specific heats and axial velocities since the zone of "intensive" heat exchange is typically small. Therefore, the heat balance equations are independent of each other.

Variation of temperature over the volume of the apparatus is described by the heat balance equation. Since the process involves heat exchange between two phases we should write down independent equations for each phase. The equation of heat balance (per unit time) for the elementary volume dv of the apparatus can be written as

$$dQ_1 = (dQ_2 - dQ_2') + (dQ_3 - dQ_3') - dQ_4 + dQ_5 \qquad \text{(VI.60)}$$

where Q_1 is the accumulated heat, Q_2 is the heat supplied to the volume owing to convection, Q_2' is the heat removed from the volume

owing to convection, Q_3 is the heat supplied to the volume owing to heat conductivity, Q_3' is the heat removed from the volume owing to heat conductivity, Q_4 is the heat removed from the volume owing to the endothermic physico-chemical processes, and Q_5 is the heat supplied to the volume from the external sources.

We can make the following approximations in Eq. (VI.60). The process may be assumed to be a steady-state one ($dQ_1 = 0$), the heat transfer owing to heat conductivity may be neglected ($dQ_3 - dQ_3' = 0$) and the heat of the physico-chemical process may also be ignored ($dQ_4 = 0$). Then Eq. (VI.60) can be written as

$$dQ_5 = -(dQ_2 - dQ_2') \qquad \text{(VI.61)}$$

The heat losses through the reactor walls in the industrial cracking apparatus are typically not more than 4% so that we can assume that the reactor is adiabatic and dQ_5 is the heat transferred from the heated surface of the catalyst to the gas mixture.

Hence we obtain

$$dQ_2 - dQ_2' = d(GTc)\, d\tau$$

and

$$dQ_5 = \alpha \frac{F}{v} (T_{ext} - T)\, dv\, d\tau$$

where F is the heat-exchange surface area (m^2), that is the surface area of the catalyst beads, and T_{ext} is the temperature of the external flow.

Since the parameters $G_{cat}c_{cat}$ and $G_m c_m$ are practically constant we can write the following heat balance equations: for the catalyst

$$\frac{dT_{cat}}{dv} = \frac{1}{G_{cat}c_{cat}} \alpha \frac{F}{v} (T_m - T_{cat}) \qquad \text{(VI.62)}$$

for the gas mixture

$$\frac{dT_m}{dv} = \frac{1}{G_m c_m} \alpha \frac{F}{v} (T_{cat} - T_m) \qquad \text{(VI.63)}$$

Substitution of $\alpha \frac{F}{v} (T_{cat} - T_m)$ from Eq. (VI.63) in Eq. (VI.62) yields

$$G_{cat}c_{cat}\, dT_{cat} = -G_m c_m\, dT_m \qquad \text{(VI.64)}$$

Integration of Eq. (VI.64) for T_{cat} between T_{cat}^i and T_{cat} and for T_m between T_m^i and T_m yields

$$G_{cat}c_{cat}(T_{cat}^i - T_{cat}) = G_m c_m (T_m - T_m^i) \qquad \text{(VI.65)}$$

The heat equilibrium temperature T_e ($T_{cat} = T_m = T_e$) is given by the following equation:

$$T_e = \frac{G_{cat}c_{cat}T^i_{cat} + G_m c_m T^i_m}{G_{cat}c_{cat} + G_m c_m} \quad \text{(VI.66)}$$

The volume of the "intensive" heat exchange after which the catalyst temperature is $T_e + 1$ can be found by integrating Eq. (VI.62). Eq. (VI.65) yields

$$T_m - T_{cat} = \frac{G_{cat}c_{cat}T^i_{cat} + G_m c_m T_m}{G_m c_m} - \frac{G_{cat}c_{cat} + G_m c_m}{G_m c_m} T_{cat} \quad \text{(VI.67)}$$

Substitution of Eq. (VI.67) in Eq. (VI.62) and integration between T^i_{cat} and $T_e + 1$ and 0 and v_{int} yield

$$v_{int} = \frac{1}{\alpha \frac{F}{v}} \cdot \frac{1}{\frac{1}{G_m c_m} + \frac{1}{G_{cat}c_{cat}}} \ln \frac{T^i_m - T^i_{cat}}{\frac{G_{cat}c_{cat}}{G_m c_m}(T^i_{cat} - T_e - 1) - (T^i_m - T_e - 1)} \quad \text{(VI.68)}$$

The surface area F/v per unit volume for the catalyst beads is given by the following equation (see also Eqs. (VI.57) and (VI.58):

$$F/v = 6/d_e(1 - \varepsilon) = 6 \times 0.5/3 \times 10^{-3} = 10^3 \text{ m}^2/\text{m}^3$$

Eq. (VI.66) yields $T_e = (27.0 \times 1000 \times 783 + 13.5 \times 3000 \times \times 748)/(27.0 \times 1000 + 13.5 \times 3000) = 762$ K.

Hence, Eq. (VI.68) yields $v_{int} = 0.1$ m^3 which is less than 1% of the total reaction volume. Thus, in calculations we can assume that the thermal equilibrium between catalyst and the gas mixture is established immediately and T_e is the starting temperature of the process.

Problem 17 (see [23], pp. 265-278). Catalytic oxidation of SO_2 into SO_3 is carried out in a reactor with four fluidized beds of vanadium catalyst. The starting gas contains $a = 11\%$ of SO_2, $b = 10\%$ of O_2 and 79% of N_2. The overall degree of conversion is $x = 0.97$. The following degrees of conversion are obtained after the catalyst beds: bed 1—0.64, bed 2—0.87, bed 3—0.94, bed 4—0.97.

(1) Plot the optimum and equilibrium functions $x(T)$ and the isotherms for each catalyst bed.

(2) Calculate the reaction rate constant and the approximate catalyst volumes for the first and second catalyst beds. The gas flow rate through the first catalyst bed is 31 000 m^3/h. The reserve factors are 1.1 for the first bed and 1.2 for the second bed.

(3) Calculate the surface areas of the heat exchangers in the second catalyst bed from the following data on the gas components (their

flow rates V and specific heats c).

Parameter	SO_2	O_2	N_2	SO_3
V (m^3/s)	0.35	0.57	7.03	0.63
c (kJ/m^3 K)	2.05	1.38	1.34	—

The physical and hydrodynamic parameters of the second catalyst bed: Ar = 2.26×10^4 (see Problems 14 and 15), the diameter of the catalyst particles $d = 1.5 \times 10^{-3}$ m. The heat conductivity of the gas is $\lambda = 6 \times 10^{-2}$ J/m s K. The kinematic viscosity of the gas is $\nu = 6.6 \times 10^{-5}$ m^2/s. The heat exchanger consists of steel pipes with the diameter $d_p = 35 \times 10^{-3}$ m and the wall thickness $\delta = 2.5 \times 10^{-3}$ m. The heat conductivity of the pipe walls is $\lambda_w = 46.4$ J/m s K. The initial temperature of the cooling water is $t_1 = 15$ °C; the final temperature of the cooling water is $t_f = 80$ °C; the mean water temperature is $t = (t_1 + t_f)/2 = 47.5$ °C. The viscosity of water is $\mu_w = 0.57 \times 10^{-3}$ Pa s, the heat conductivity of water is $\lambda_w = 6.45$ J/m s K. The gas density is $\rho_g = 3.74$ kg/m^3. The velocity of the cooling water is $w_w = 0.4$ m/s.

Solution. (1) Oxidation of SO_2 into SO_3 is a reversible exothermic reaction. The x *vs.* t (or u *vs.* t) plot for this reaction exhibits a maximum (see Chapter IV, Fig. 3). The optimum temperature of the reaction is found from the equation for the maximum of the function $x = f(T)$:

$$\left(\frac{d\frac{dx}{d\tau}}{dT}\right)_{x=\text{const}} = 0$$

$$T_{opt} = T_e + \Delta T = \frac{T_e}{1 + \frac{2.3RT_e}{mq_r} \log \frac{E + mq_r}{E}} \qquad \text{(VI.69)}$$

Here T_e is the equilibrium temperature corresponding to the given x, q_r is the reaction heat, E is the activation energy of the reaction, and m is the reaction order with respect to the main component.

Calculation of the optimum temperature of the reversible exothermic reaction has been described also in Chapter IV (Problem 11).

To transform Eq. (VI.69) for T_{opt} we shall make use of the temperature dependence of the equilibrium constant K_p:

$$\log K_p = \log K_p^0 + q_r/2.3T_e$$

and the formula expressing K_p in terms of the initial concentrations of SO_2 and O_2 (a and b) (in % by volume) and the degree of conversion x which is written for $P = 10^5$ Pa as:

$$\log K_p = \log \frac{x}{(1-x)\sqrt{\frac{b - 0.5ax}{100 - 0.5ax}}} \qquad \text{(VI.70)}$$

The resulting equation for T_{opt} has the following form

$$T_{opt} = \frac{\frac{q_r}{2.3P}}{\log \frac{x}{(1-x)\sqrt{\frac{b-0.5ax}{100-0.5ax}}} - \log K_p^0 + \frac{1}{m} \log \frac{E+mq_r}{E}} \qquad \text{(VI.71)}$$

If $q_r/2.3P = 4905$ we have $\log K_p^0 = -4.64$. Since the activation energy for the vanadium catalyst is $E = 87\,900$ kJ/kmole (21 000 kcal/kmole) and the reaction order is $m = 2$ we obtain

$$T_{opt} = \frac{4905}{\log \frac{x}{(1-x)\sqrt{\frac{b-0.5ax}{100-0.5ax}}} + 4.937}$$

For the first catalyst bed we obtain

$$T_{opt_1} = \frac{4905}{\log \frac{0.64}{(1-0.64)\sqrt{\frac{10-0.5\times 11\times 0.64}{100-0.5\times 11\times 0.64}}} + 4.937} = 850 \text{ K}$$

The optimum temperatures for other catalyst beds are calculated in a similar way. The equilibrium degree of conversion can be found from Eq. (V.37):

$$x_e = \frac{K_p}{K_p + \sqrt{\frac{100-0.5ax_e}{P(b-0.5ax_e)}}}$$

The equilibrium constant at 660-800 K can be found from Eq. (V.34): $\log K_p = 4905/T - 4.64$. For the first catalyst bed we obtain $\log K_p = 4905/850 - 4.64 = 1.13$ and $K_p = 13.5$. Hence we find $x_e = 0.775$ for the first bed. Similar calculations should be made for other catalyst beds. The results are given below:

Bed	1	2	3	4
x	0.64	0.87	0.94	0.97
x_e	0.775	0.928	0.968	0.984
K_p	13.5	55	126	276
T_{opt} (K)	850	770	730	695
T_{opt} (°C)	577	497	457	422

These results are used to plot x as a function of temperature (Fig. 20).

(2) The reaction rate constant at $T = 793$ K is known to be 5.45. We can find the reaction rate constant at $T = 850$ K from Eq. (IV.27). Since the activation energy is $E = 87\,900$ kJ/kmole we have $k = 5.45 \exp((87\,900/8.31)(1/793 - 1/850)) = 13.7$.

To calculate the time τ_1 of contact between the gas and the catalyst in the first catalyst bed we can make use of the approximate

equation

$$\tau = \frac{ax}{k\left(\frac{x_e - x}{x}\right)^{0.8}\left(b - \frac{ax}{2}\right)\beta} \qquad \text{(VI.72)}$$

where the factor β takes into account variation of the concentration of SO_2 owing to the decrease of the volume of the reaction mixture: $\beta = 1/(1 - ax/200)$; a (% by volume) is the initial concentration of SO_2, and b (% by volume) is the initial concentration of O_2.

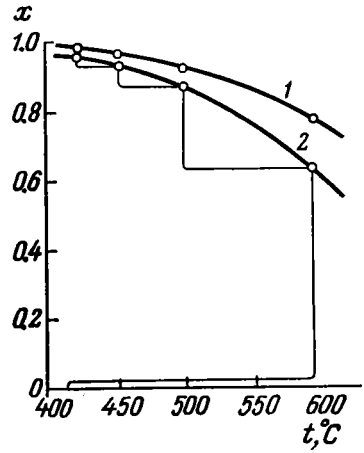


Fig. 20. The degree of conversion x as a function of temperature t for oxidation of SO_2 to SO_3 in a four-bed reactor
1—equilibrium plot; *2*—optimum plot.

Assuming the complete-mixing conditions in the first catalyst bed we obtain $\tau_1 = 0.27$ s.

The volume of the first catalyst bed is $v_{cat\ 1} = 1.1 \times 31\,000 \times \times 0.27 \times 850/3600 \times 273 = 7.9$ m³.

The hydrodynamic conditions in the second and other catalyst beds are close to the plug-flow conditions. The time of contact between the gas and the catalyst in these beds can be calculated from the kinetic equation for the filter bed with a correction factor η which takes into account the decrease in the process rate (the driving force ΔC) owing to mixing and slippage of the gas.

The Boreskov's equation for the filter bed of the vanadium catalyst (V.35) can be used for the second catalyst bed:

$$u = \frac{dx}{d\tau} = \frac{k}{2a}\left(\frac{x_e - x}{x}\right)^{0.8}(2b - ax)$$

and

$$\tau_2 = \eta \frac{2a}{k_2} \int_{0.64}^{0.87} \left(\frac{x_2}{x_{e2} - x_2}\right)^{0.8} \frac{dx_2}{2b - ax_2}$$

The factor η is given by the empirical formula:

$$\eta = \frac{1}{1 - \left(\frac{x_i - x_{i-1}}{1 - x_i}\right)^5} \qquad \text{(VI.73)}$$

Here x_i is the degree of conversion in the given bed and x_{i-1} is the degree of conversion in the preceding bed.

The time τ_2 is found by graphical integration technique as described in Chapter V (Problem 1). At the temperature 770 K we have

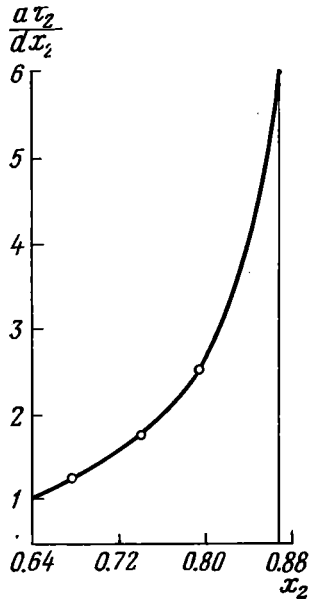


Fig. 21. Determination of the contact time in the second catalyst bed in Problem 17.

$k = 3.5$] and $\eta = 1/(1 - ((0.87 - 0.64)(1 - 0.64))^5) = 1.12$ so that we obtain $1/u_2 = d\tau_2/dx_2 = (2 \times 11/3.5)(0.87/(0.928 - 0.87))^{0.8}(1/(2 \times 10 - 11.087))\,1.12$. Given below are the results for arbitrary values of x_2:

x_2	0.64	0.69	0.74	0.79	0.84	0.87
$dx_2/d\tau_2$	1.09	1.33	1.76	2.5	4	5.9

These results are used to plot $d\tau_2/dx_2$ as a function of x_2 (see Fig. 21) which yields the theoretical time of contact in the second catalyst bed: $\tau_2 = 0.545$ s. Hence, we obtain

$$v_{cat2} = 1.2 \times 31\,000 \times 0.545 \times 770/273 \times 3600 = 15.7 \text{ m}^3$$

The times of contact and the catalyst volumes for the other catalyst beds are calculated in a similar way.

(3) We shall calculate the parameters of the heat exchanger for the second fluidized bed since in the first catalyst bed the optimum

temperature is maintained by decreasing the heat delivered with the initial gas mixture whose temperature can be considerably lower than the activation temperature of the catalyst (owing to rapid equalization of temperature in the fluidized bed).

The amount Q_h of heat which should be removed from the catalyst bed by the heat exchanger is found from the heat balance equation for the second bed:

$$Q_1 + Q_r = Q_2 + Q_{loss} + Q_h$$

The heat Q_1 delivered with the gases to the second bed is

$$Q_1 = (V_{SO_2} c_{SO_2} + V_{O_2} c_{O_2} + V_{N_2} c_{N_2}) T_{opt1} = 11\,120 \text{ kJ/s}$$

The optimum temperature for each bed and the respective degrees of conversion are given above in section (1). The heat of the reaction in the second bed is given by the empirical equation $q_2 = 101\,430 - 9.25 T_{opt2} = 94\,310$ kJ/kmole. Hence we have

$$Q_{r2} = q_2 V_{SO_2} (x_2 - x_1)/22.4 = 0.35 (0.87 - 0.64) \times \times 94\,310/22.4 = 950 \text{ kJ/s}$$

The heat losses Q_{loss} in each bed can be found from the approximate empirical equation (VI.74) and it is assumed that for each catalyst bed in the reactor the heat insulation surface area is $S_{ins} = 50$ m², the temperature of the heat insulation is $t_{ins} = 50$ °C, and the temperature of the air is $t_{air} = 15$ °C:

$$Q_{loss} = S_{ins} \alpha_{ins} (t_{ins} - t_{air}) \qquad \text{(VI.74)}$$

The heat transfer coefficient for the heat insulation surface is given by the following empirical equation:

$$\alpha_{ins} = 9.74 + 0.07 (t_{ins} - t_{air}) = 12.2 \text{ J/s m}^2 \text{ K}$$

Hence, $Q_{loss} = 21$ kJ/s.

The heat Q_2 removed from the second bed with the gas mixture can be found as it was done for Q_1 : $Q_2 = 10\,220$ kJ/s. Hence, the heat Q_h which should be removed is $Q_h = 11\,120 + 950 - 10\,220 - 21 = 1829$ kJ/s.

The surface area F_h of the heat exchanger in the second bed can be found from Eq. (VI.35):

$$F_h = Q_h / k_{T_2} \Delta T_2$$

The heat transfer coefficient is given by Eq. (VI.38):

$$k_{T_2} = \frac{1}{\frac{1}{\alpha_{susp}} + \frac{\delta_w}{\lambda_w} + \frac{1}{\alpha_{cool}}}$$

The coefficient α_{susp} of the convective heat transfer from the fluidized bed to the heat-exchanger surface can be calculated from

Eq. (VI.39) for the high-turbulence regime:

$$Nu_2 = Nu_{max} = 0.86\,Ar^{0.2} = 0.86\,(2.26 \times 10^4)^{0.2} = 6.36$$

and

$$\alpha_{susp} = Nu_{max}\,\lambda_g/d_{cat} = 224\ J/s\,m^2\,K$$

The coefficient α_{cool} of the convective heat transfer from the heat-exchanger wall to the cooling water is given by the following equation:

$$Nu_{cool} = \alpha_{cool} d_p/\lambda_{cool} = 0.021\,Re_{cool}^{0.8}\,Pr^{0.43} \qquad (VI.75)$$

We obtain $Re_{cool} = w_w d_p \rho_w/\mu_w = 0.4 \times 35 \times 10^{-3} \times 10^3/0.57 \times 10^{-3} = 24.6 \times 10^3$, $Nu_{cool} = 0.021\,(24.6 \times 10^3)^{0.8}\,3.74^{0.43} = 123$, and $\alpha_{cool} = 2230\ J/m^2\,s\,K$. Hence, $k_{T_2} = 224\ J/m^2\,s\,K$. The temperature difference between the bed temperature of 497 °C and the mean temperature of the cooling water (47.5 °C) is 450 °C. Thus, $F_h = 1829 \times 10^3/224 \times 450 = 18.1\ m^2$.

The heat-exchange surface areas for other catalyst beds can be found by similar calculations.

Problem 18 (modified from [23]). Approximate calculations for the ammonia synthesis column.

Ammonia is synthesized in a reactor (column) with fluidized catalyst beds. The fine-pore iron catalyst is promoted with Al_2O_3, K_2O, CaO, and SiO_2. The temperature range of the stable operation of the catalyst is 475-540 °C. The density of the catalyst particles $\rho_{cat} = 3500\ kg/m^3$. The number of the catalyst beds is five providing for close to optimum conditions of synthesis.

The following particle sizes were selected for the catalyst bed (proceeding from the hydrodynamic considerations): $d_1 = d_2 = 1.5$ mm; $d_3 = d_4 = 2.0$ mm; $d_5 = 2.5$ mm (d is the particle diameter).

Ammonia is synthesized under the pressure 3×10^7 Pa with secondary condensation. The composition of the initial nitrogen-hydrogen mixture is close to the stoichiometric ratio. The concentration of the inert admixtures in the gas (CH_4 and Ar) is $C_{in} = 0.96\%$ by volume. The dynamic viscosity of the gas mixture at 3×10^7 Pa is $\mu \approx 3.0 \times 10^{-5}$ Pa s. Table 38 presents the material balance data for the above conditions (see Chapter II, Problem 1).

1. Find the ammonia concentration x_e in the equilibrium gas mixture in the given temperature range and plot the equilibrium curve and the optimum temperature curve.

2. Calculate the critical and operational velocities of the gas and the cross section of the catalyst bed.

3. Calculate the reaction rate constants, the heights of the catalyst beds and the total volume of catalyst, and the hydraulic resistance of the catalyst beds.

TABLE 38

Material Balance of Ammonia Synthesis

	Gas components	Content, % by volume	Flow rate V_g, m³/s
Entry to bed 1	NH_3	4.00	0.93
	H_2	71.28	16.73
	N_2	23.76	5.55
	CH_4+Ar	0.96	0.22
	Total:	100	23.45
Exit from bed 1 and entry to bed 2	NH_3	10.50	2.32
	H_2	66.40	14.67
	N_2	22.12	4.89
	CH_4+Ar	0.98	0.22
	Total:	100	22.10
Exit from bed 2 and entry to bed 3	NH_3	13.50	2.90
	H_2	64.10	13.76
	N_2	21.38	4.61
	CH_4+Ar	1.02	0.22
	Total:	100	21.50
Exit from bed 3 and entry to bed 4	NH_3	16.50	3.46
	H_2	61.84	12.96
	N_2	20.61	4.32
	CH_4+Ar	1.05	0.22
	Total:	100	20.96
Exit from bed 4 and entry to bed 5	NH_3	19.50	3.98
	H_2	59.57	12.19
	N_2	19.85	4.06
	CH_4+Ar	1.08	0.22
	Total:	100	20.45
Exit from bed 5 (from reactor)	NH_3	22.50	4.50
	H_2	57.30	11.41
	N_2	19.10	3.80
	CH_4+Ar	1.10	0.22
	Total:	100	19.93

Solution. 1. The equilibrium constant for the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3 + q$ is given by Eq. (II.7) as a function of temperature: $\log \sqrt{K_p} = \log \sqrt{p_{N_2} p_{H_2}^3 / p_{NH_3}^2} = -2074.8/T + 2.4943 \log T + \beta T - 1.8564 \times 10^{-7} T^2 - 2.206$. When $P = 3 \times 10^7$ Pa we have $\beta = 1.256 \times 10^{-4}$.

The values of $\sqrt{K_p}$ calculated from Eq. (II.7) for the pressure range from 10^7 to 10^8 Pa are given in Table 15 (Chapter II).

The content of ammonia x_e in the equilibrium reaction mixture (for the stoichiometric initial nitrogen-hydrogen mixture) is given by the following equation derived from the composition of the reaction mixture:

$$x_e = 1 + 1.54/P\sqrt{K_p} - \sqrt{(1 + 1.54/P\sqrt{K_p})^2 - 1} \qquad \text{(VI.76)}$$

For the above temperature range Eq. (VI.76) yields the following values * of x_e:

t, °C	450	475	500	527	550
x_e	0.358	0.315	0.264	0.21	0.198

The optimum temperatures for the above conditions (promoted iron catalyst, pressure 3×10^7 Pa) can be found from the following empirical equations:

$$x = 27 - 0.18\,(T_{opt} - 450) \qquad \text{(VI.77)}$$

or

$$T_{opt} = 873 - 5.55\,x \qquad \text{(VI.78)}$$

Table 38 gives the practical ammonia yields x, that is, the ammonia content in the gas mixture after each reactor bed.

The optimum temperatures T_{opt} found from Eq. (VI.78) and the yields for each bed are given below:

Bed	1	2	3	4	5
x_e	0.196	0.218	0.25	0.282	0.315
x	0.105	0.135	0.165	0.195	0.225
T_{opt}, °C	541	525	507	491	475

Figure 22 presents the x-t curves plotted from the above data.

2. To find the operation velocity w_g of the gas flow we have to calculate the critical velocities for suspension of the catalyst particles (w_{susp}) and removal of the particles (w_{rem}).

The parameter w_{susp} is found from Eq. (VI.29):

$$Re_{susp} = \frac{Ar}{1400 + 5.22\sqrt{Ar}}$$

The viscosity of the gas mixture is $\mu = 3.0 \times 10^{-5}$ Pa s.

The gas density is given by the following sum:

$$\rho_g = (\rho_{H_2} p_{H_2} + \rho_{N_2} p_{N_2} + x\rho_{NH_3} + \rho_{in} p_{in}) \frac{T_0 P}{T P_0} \qquad \text{(VI.79)}$$

The gas density is found from Eq. (VI.79) using the composition of the gas leaving each bed and the density of the inert admixtures

* The values of x_e (and K_p) can also be found in handbooks and special monographs.

is taken to be equal to that of methane. For the first bed we have $\rho_{g1} = 42.6$ kg/m^3, $Ar_1 = gd^3\rho_{g1}(\rho_{cat} - \rho_g)/\mu^2 = 55 \times 10^5$ and $Re_{susp\ 1} = 405$. Hence, we obtain

$$w_{susp1} = Re_{susp1}\,\mu/d_1\,\rho_{g1} = 0.19 \text{ m/s}$$

The parameter w_{rem} is given by Eq. (VI.33):

$$Re_{rem} = \frac{Ar_{min}}{18 + 0.61\sqrt{Ar_{min}}}$$

If $d_{min} = 0.5$ mm we have $Ar_{min} = 2 \times 10^5$, $Re_{rem} = 690$, and $w_{rem} = 0.97$ m/s.

The velocity of the gas flow in the reactor is selected according to the conditions of the last catalyst bed where w_{g5} is taken to be

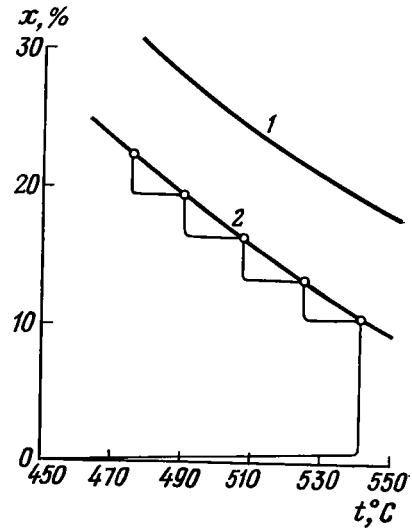


Fig. 22. The degree of conversion x as a function of temperature t for ammonium synthesis in a five-bed reactor
1—equilibrium plot; *2* — optimum plot.

close to w_{susp5} while the gas velocity in the lower bed is higher owing to a higher gas flow rate V_g. This is done to provide for full suspension of particles in the lower beds where the catalyst particles of smaller diameter are loaded owing to the same reasons.

For the bed 5 we obtain $\rho_{g5} = 51.3$ kg/m^3, $Ar_5 = 224 \times 10^5$, $Re_{susp5} = 590$, and $w_{susp5} = 0.22$ m/s. The operational gas velocity in the bed 5 is taken to be $w_{g5} = 1.18 w_{susp5} = 0.26$ m/s. At such gas velocity the conditions in the bed 5 are close to the ideal plug-flow conditions decreasing mixing and bubbling of the gas and providing for increased ammonia yield.

Hence, the cross-section area of the catalyst bed is $S_{cat} = V'_{g5}/w_{g5}$ where V'_{g5} is the gas flow rate (in m^3/s) in the bed 5 under operational

conditions. We have

$$V'_{g5} = V_{g5} T_5/T_0 P = 19.93 \times 748/273 \times 300 = 0.182 \text{ m}^3/\text{s}$$

$$S_{cat} = 0.182/0.26 = 0.705 \text{ m}^2$$

The diameter of the catalyst bed is $1.13 \sqrt{S_{cat}} = 0.95$ m. The internal diameter of the column for ammonia synthesis can be taken to be 1 m.

3. The reaction rate constant for ammonia synthesis on promoted iron catalyst can be found from the modified Arrhenius equation (IV.27):

$$k = 3.485 \times 10^{19} \beta \frac{1}{T} e^{-E/RT} \qquad \text{(VI.80)}$$

Here β is a dimensionless factor depending on the reaction conditions. For $P = 3 \times 10^7$ Pa and $t = 470$-550 °C we have $\beta \approx 0.8$. The activation energy E for the commercial iron catalyst is about 170 kJ/mole. Given below are the reaction rate constants found from Eq. (VI.80) for the above-calculated optimum temperatures:

T_{opt}, K	814	798	780	764	748
k	24.2×10^4	16.1×10^4	8.4×10^4	4.6×10^4	2.96×10^4

The rate of ammonia synthesis over the iron catalyst under the conditions close to equilibrium is given by Eq. (IV.35):

$$u = u_1 - u_2 = \frac{dp_{NH_3}}{d\tau} = k_1 p_{N_2} \left(\frac{p^3_{H_2}}{p^2_{NH_3}} \right)^{0.5} - k_2 \left(\frac{p^2_{NH_3}}{p^3_{H_2}} \right)^{0.5}$$

Here k_1 and k_2 are the rate constants for synthesis and dissociation of ammonia and p_{NH_3}, p_{H_2}, and p_{N_2} are the partial pressures of the gas components.

Equation (IV.35) can be written in a form more convenient for calculations. The concentrations of the gas components are expressed in terms of the degree of conversion and the total gas pressure, and the time of contact τ between the gas and the catalyst is expressed in terms of the mean mass flow rate G_g, the gas density and the cross section of the reactor.

The modified kinetic equation also takes into account the content of inert components in the gas. The equation is written as

$$u = \frac{dx}{dH_0} = \frac{k\rho_g}{(1 - C_{in})^{1.5} P^{0.5} G_g} \left[\frac{x_e^2}{(1 - bx_e)^4} - \frac{x^2}{(1 - bx)^4} \right] \times$$

$$\times \frac{(1 - bx)^{2.5}}{x} (1 + x)^3 \qquad \text{(VI.81)}$$

Here H_0 is the height of the stationary catalyst bed providing for a given time of contact between the gas and the catalyst (m), ρ_g is the density of the gas mixture (kg/m^3), G_g is the mean mass flow

rate (kg/m² h)

$$G_g = 3600\, V_g\, \rho_g / S_{cat} \qquad \text{(VI.82)}$$

C_{in} is the concentration of the inert components in the starting gas (relative units), and $b = (1 + C_{in})/(1 - C_{in})$.

The differential equation (VI.81) describes the kinetics of ammonia synthesis under the conditions of ideal plug flow. Empirical results suggest that the first four fluidized catalyst beds in the ammonia synthesis column function under the conditions close to complete mixing. The height of the catalyst bed under the complete-mixing conditions can be found from Eqs. (VI.81) and (VI.82):

$$H_0 = \frac{3600\, \Delta x\, V_g\, P^{0.5}}{k S_{cat}} \cdot \frac{x\,(1-C_{in})^{1.5}}{(1-bx)^{2.5}\,(1+x)^3} \cdot \frac{1}{\left[\dfrac{x_e^2}{(1-bx_e)^4} - \dfrac{x^2}{(1-bx)^4}\right]} \qquad \text{(VI.83)}$$

Here $\Delta x = x_i - x_{i-1}$ and x_i is the NH_3 content in the gas mixture after the ith catalyst bed.

For the first catalyst bed we have $x_1 = 0.105$, $x_{e1} = 0.196$, $\Delta x_1 = 0.105 - 0.040 = 0.065$, $C_{in} = 0.01$, $b_1 = 1.01/0.99 = 1.02$, $k_1 = 24.2 \times 10^4$, $V_{g1} = 22.1$ m³/s, and $H_{01} \approx 0.69$ m.

Similar calculations for other catalyst beds yield $H_{02} = 0.47$ m, $H_{03} = 0.82$ m, and $H_{04} = 1.03$ m.

As mentioned above the hydrodynamic conditions in the bed 5 are close to the ideal plug flow. We shall calculate H_{05} by graphical integration of Eq. (VI.81) written in the form

$$\frac{dH_0}{dx} = \frac{3600\, V_g\, P^{0.5}}{k S_{cat}} \cdot \frac{x\,(1-C_{in})^{1.5}}{(1-bx)^{2.5}\,(1+x)^3} \cdot \frac{1}{\left[\dfrac{x_e^2}{(1-bx_e)^4} - \dfrac{x^2}{(1-bx)^4}\right]} \qquad \text{(VI.84)}$$

Taking the x values of 0.195, 0.205, 0.215, and 0.225 we obtain the following values of dH_{05}/dx from Eq. (VI.84):

x	0.195	0.205	0.215	0.225
dH_{05}/dx	31	34	37.6	42.3

These results are used to plot dH_0/dx as a function of x (Fig. 23) and to determine the height of the bed 5 as the area of the shaded region in the plot. We obtain $H_{05} = 1.05$ m.

The catalyst volume in each bed is given by the formula

$$v_{cat} = c H_0 S_{cat} \qquad \text{(VI.85)}$$

where c is the factor taking into account the losses of the catalyst owing to its attrition and poisoning which are higher in the first two catalyst beds. According to the selected values of the factor c we obtain

Bed	1	2	3	4	5
c	1.35	1.35	1.1	1.1	1.2
v_{cat}, m³	0.66	0.45	0.71	0.89	0.94

The total volume of the catalyst in the reactor is $v_{cat} = 3.65$ m³.

The hydraulic resistances of the catalyst beds can be found from Eq. (VI.42)

$$\Delta P = g \rho_{cat} H (1 - \varepsilon)$$

where $H = cH_0$.

If the bed porosity is $\varepsilon = 0.4$ we obtain the following hydraulic resistance for the beds from 1 to 5, respectively: 19 200, 13 100,

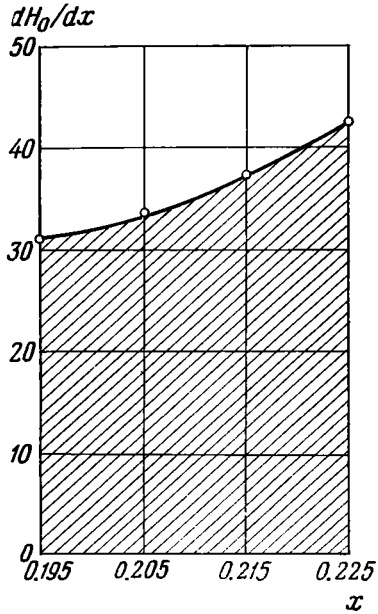


Fig. 23. Determination of the height of the fifth catalyst bed in Problem 18.

20 800, 26 000, and 27 400 Pa. The total hydraulic resistance of the catalyst beds is the sum of resistances of individual beds or $\Delta P = v_{cat}\rho_{cat}g\ (1 - \varepsilon)/S_{cat} = 1.065 \times 10^5$ Pa.

Further Problems for Students

1. Calculate the volume of catalyst for oxidation of SO_2 to SO_3 if the time of contact between the gas and the catalyst is 0.55 s. The porosity of the catalyst bed is 0.364. The temperature in the reaction zone is 550 °C and the gas flow rate is 10 300 m³/h.
2. Find the gas flow rate in the reactor for oxidation of SO_2 if the gas velocity is 0.8 m/s, the reactor diameter is 3 m, the height of the catalyst bed is 300 mm, and the temperature in the reactor is 500 °C.

3. Calculate the increase in the temperature of the air-SO_2 mixture with oxidation of SO_2. The degree of oxidation is 0.01, the starting gas contains 5% (by volume) of SO_2, the reaction heat is (102 500 — — 9.26T) kJ/kmole and the components of the starting gas have the following specific heats (kJ/m^3 K): O_2—1.4, N_2—1.33, and SO_2—2.03.

4. Find the productivity of the catalyst for ammonia synthesis (in kg of NH_3 per hour per litre of catalyst) if the flow rate of the nitrogen-hydrogen mixture is 20 000 m^3/h per 1 m^3 of catalyst, the ammonia content in the final gas mixture is 20% by volume, and the catalyst volume is 1.5 m^3.

5. Calculate the productivity of the catalyst for ammonia synthesis (in kg of NH_3 per hour per m^3 of catalyst) if the ammonia content is 2.7% by volume in the starting mixture and 26.5% by volume in the final mixture and the gas flow rate is 45 000 m^3/h.

6. Calculate the productivity of the reactor for catalytic oxidation of methanol to formaldehyde in a fluidized catalyst bed (silver on pumice) if the starting alcohol-air mixture contains 35% methanol. The process involves two reactions:

$$CH_3OH + 0.5O_2 = CH_2O + H_2O \quad (1)$$

$$CH_3OH \rightarrow CH_2O + H_2 \quad (2)$$

The degree of conversion of methanol to formaldehyde is 70%. The reaction (1) consumes 75% of converted methanol and the remaining 25% is consumed in the reaction (2). The temperature of the process is 600 °C, the catalyst particles have the diameter of 2.5 mm. The density of the catalyst is 10 680 kg/m^3. The density of the gas under the conditions of the process is 4.12 kg/m^3. The kinematic viscosity of the gas is 8.07 $\times$ 10^{-5} m^2/s. The product is obtained as formaldehyde solution in water (formalin) with the concentration 40% by mass.

7. The catalytic reaction A $\rightarrow$ R is carried out under the ideal plug-flow conditions in the experimental reactor containing 10 cm^3 of the catalyst. The consumption of the component A is 20 litre/h, the pressure is 2.5 $\times$ 10^5 Pa, and the temperature is 125 °C. The reaction mixture is recycled through the reactor. The experimental results are given in Problem 8 (Chapter VI). Calculate the reaction order and the reactor volume providing for the degree of conversion 0.35.

8. The catalytic reaction A $\rightarrow$ R is analysed in an experimental ideal plug-flow reactor with varying amounts of the catalyst. The consumption of the component A is 20 litre/h, the temperature is 117 °C, and the pressure is 3 $\times$ 10^5 Pa. The final reaction mixture contained the following concentrations C_A of A:

Catalyst volume, cm^3	20	40	80	120	160
C_A, mole/litre	0.074	0.06	0.044	0.035	0.029

Calculate the catalyst volume providing for the degree of conversion 0.35 if the consumption of A is 2000 mole/h at the above pressure and temperature.

9. The process of catalytic oxidation of SO_2 to SO_3 is carried out in the one-stage ideal plug-flow reactor with a filter bed of vanadium catalyst. The reactor's productivity is 75 tons of sulphuric acid (monohydrate) per day. The starting gas has the following composition (in % by volume): SO_2—11, O_2—10, N_2—79. The specified degree of oxidation is 0.75. The temperature is 570 °C. The linear velocity of gas is 1 m/s, the equilibrium degree of oxidation is 0.78. Calculate the time of contact between the gas and the catalyst, the catalyst volume, the height of the catalyst bed, the diameter of the reactor, and the time of contact for the process with the same parameters carried out under the conditions close to complete mixing (fluidized bed).

10. The reaction $3H_2 + CO \rightleftarrows CH_4 + H_2O$ is carried out over the nickel catalyst with the bulk density 480 kg/m^3. The initial reaction rate is described by the equation $u = 1.1p_{CO}(p_{H_2})^{0.5}/(1 + 1.5p_{H_2})$. The specified degree of conversion under the conditions when this equation is valid is 0.3. Calculate the volume of the catalyst for conversion of 4.536 kmoles of CO per hour if the mixture contains equimolar amounts of methane and hydrogen.

Chapter VII

Mass-transfer Processes

Introduction

Most industrial chemical processes are heterogeneous processes. The heterogeneous processes are not easy to classify owing to their enormous diversity. A conventional approach to the classification of the heterogeneous processes is to divide them into classes according to the phase states of the reactants, for instance, processes in the systems gas (G)-liquid (L), L-solid (S), G-S, etc.

The mechanisms of the heterogeneous processes are generally more complicated than those of the homogeneous processes because the reaction between reactants of different phases is preceded by delivery of reactants to the phase interface and by mass transfer between the phases. Thus, the heterogeneous process consists of a series of interrelated physico-chemical phenomena and chemical reactions. To give a quantitative description of a complex technological process it may be sometimes divided into individual stages and each stage may be analysed separately. This analysis can be used for instance to determine whether the process is diffusion limited or kinetics limited so that if the rates of the chemical reactions and the diffusion rate are incommensurable, the appropriate stage of the process may be ignored in calculations.

The reactants are delivered to the reaction zone and the reaction products are removed from it by molecular diffusion or convection. Convective mass transfer is known also as the turbulent diffusion if the reactants are highly mixed. In the two-phase or multiphase systems the reactants can be delivered to the reaction zone by absorption, adsorbtion or desorption of gases, condensation of vapours, melting or dissolution of solids, evaporation of liquids or sublimation of solids. Mass transfer between phases is, generally, a complicated diffusion process.

The important characteristics of the technological processes are the equilibrium product yield determined by the state of equilibrium under the given conditions and the actual product yield (efficiency) which is determined both by the equilibrium and the process rate.

The equilibrium of heterogeneous processes is determined by the equilibrium constant of the chemical reactions occurring in one of the phases (see Chapter II) as is the case for the homogeneous processes.

The equilibrium concentrations of the components in contacting phases are determined by the distribution law which establishes

a permanent relationship between the equilibrium concentrations of a component in two phases of the system at a given temperature. This relationship is not violated by a change in the initial concentration of the component or the overall pressure in the system. There are different forms of the distribution law describing various phase systems. For instance, the equilibrium distributions in the G-L systems are known as Henry's law and Raoult's law.

For the absorption and desorption processes the equilibrium between gases and their solutions in liquids is described by Henry's law:

$$p^* = \psi C_l^* \tag{VII.1}$$

where p^* is the equilibrium partial pressure of the absorbed gas component (Pa), C_l^* is the equilibrium solubility of the gas component in the liquid (molar fractions), and ψ is the Henry's law coefficient with the dimension of pressure.

In calculations of the absorption and desorption equilibrium the compositions of the liquid and gas are often expressed in terms of the relative molar concentrations so that Eq. (VII.1) is transformed into

$$C'_g = \psi C'_l \tag{VII.2}$$

where C'_g is the relative concentration of the dissolving gas component in the gas at equilibrium (kmoles per kmole of the neutral gas)

$$C'_g = \frac{C_g^*}{1 - C_g^*} \tag{VII.3}$$

C'_l is the relative molar concentration of the gas component in the liquid (kmoles per kmole of the liquid)

$$C'_l = \frac{C_l^*}{1 - C_l^*} \tag{VII.4}$$

C_l^* and C_g^* are the molar fractions of the dissolving gas component in the liquid and in the gas, respectively, and

$$\psi = C'_g / C'_l \tag{VII.5}$$

is the distribution coefficient which is a dimensionless parameter used in calculations as a similarity criterion.

The temperature dependence of solubility is described by the following thermodynamic equation:

$$\log \frac{\psi_1}{\psi_2} = -\frac{\Delta H}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{VII.6}$$

Here ΔH is the dissolution heat which is constant in a certain temperature range. Calculation of solubility in the framework of the theory of solutions is discussed, for instance, in the monograph [28].

The equilibrium of the chemisorption processes, for instance, when a gas dissolved in a liquid reacts with it can be found if the equilibrium constant of the reaction is known. For example, if the reversible reaction between the absorbed component A and the active component of the solvent B gives rise to the product D

$$A + B \rightleftarrows D$$

and if the system satisfies Henry's law (for low concentrations of the dissolved component) the phase equilibrium constant taking into account the chemical reaction is given by

$$\psi' = \frac{\psi}{1 + K_p C_B} \tag{VII.7}$$

where K_p is the equilibrium constant of the chemical reaction and C_B is the concentration of the active component B in the solvent.

If the gas A is absorbed by a solution of the chemisorbent B with the reaction

$$aA + bB \rightleftarrows cC + dD$$

where a, b, c, and d are the stoichiometric factors the equilibrium constant is given by

$$K_p = \frac{\left(\frac{c}{a} X_{chem}\right)^{c/a} \left(\frac{d}{a} X_{chem}\right)^{d/a}}{(N_A - X_{chem}) \left(N_B - \frac{b}{a} X_{chem}\right)^{b/a}} \tag{VII.8}$$

where N_A and N_B are the numbers of moles of the components A and B before the reaction and X_{chem} is the number of moles of A which have reacted with the chemisorbent B at equilibrium. The quantity $X_{phys} = N_A - X_{chem}$ is the amount of the gas A physically absorbed by the solvent.

In the simplest case (when $X_{chem} \to 0$) we have $X_{phys} = p_A^*/\psi$ where ψ is the Henry's law coefficient which depends on P, T, and the composition of the solvent. In more complex cases we should take into account the coefficient ψ_{phys} which also depends on the concentration of the dissolved component A.

Typically $X_{phys} \ll X_{chem}$ so that $X_{chem} \approx X$ where X is the total amount of the dissolved component. Thus, we obtain

$$p_A^* = \frac{\psi_{phys} \left(\frac{c}{a}\right)^{c/a} \left(\frac{d}{a}\right)^{d/a} X^{(c+d)/a}}{K_p \left(N_B - \frac{b}{a} X\right)^{b/a}} \tag{VII.9}$$

The systems G-L, L-S and L-L at equilibrium should satisfy the phase rule

$$F = C + V - P \tag{VII.10}$$

where F is the number of the degrees of freedom of the system, C is the number of the individual chemical components in the system, V is the number of the external variables affecting the phase equilibrium, and P is the number of phases. The systems can be described by phase diagrams which characterize the state of the system and the phase equilibria in it as a function of its composition or external conditions.

Analysing phase diagrams we can determine the equilibrium yields of products and select the conditions for a real industrial process to carry it out as close as possible to the equilibrium.

The adsorption equilibrium in a G-S system is described by the equation for the adsorption isotherm

$$G_a = f(p)$$

One of the simplest adsorption isotherms is the Langmuir isotherm

$$G_a = \frac{ABp}{1+Ap} \qquad \text{(VII.11)}$$

where A and B are the constants depending on the properties of the adsorbate and the adsorbent, G_a is the amount of the adsorbed material per one mass (or volume) unit of the adsorbent, and p is the partial pressure of the adsorbed gas.

The equation for the adsorption isotherm can be written in the following general form:

$$G_a = A_1 \exp(-B_1 W) + A_2 \exp(-B_2 W) \qquad \text{(VII.12)}$$

Here A_1, A_2, B_1, and B_2 are the constants depending on the properties of the adsorbent and the adsorbate, T is the absolute temperature,

$$W = \frac{T^2}{\beta_a^2} \ln \frac{p_{sat}}{p}$$

$\beta_a = V_2/V_1$ is the affinity coefficient, V_1 and V_2 are the molar volumes of a standard compound and the analysed component (in the liquid state) (m^3/kmole), and p_{sat} is the saturation vapour pressure of the adsorbed component.

The adsorption isotherm of a given vapour at the temperature T_2 can be calculated from the known isotherm of the vapour of the standard compound at the temperature T_1. The relationship between the isotherms is given by the following equation:

$$\ln p_2 = \ln p_{sat2} - \beta_a \frac{T_1}{T_2} \ln \frac{p_{sat1}}{p_1} \qquad \text{(VII.13)}$$

Here p_1 and p_2 are the partial pressures of the standard compound and the analysed component (Pa), p_{sat1} is the saturation vapour pressure of the standard compound at the temperature T_1 (Pa),

and p_{sat2} is the saturation vapour pressure of the analysed component at the temperature T_2 (Pa).

The ordinates of the unknown isotherm G_2 can be found from the ordinates G_1 of the isotherm for the standard compound:

$$G_2 = G_1 \frac{1}{\beta_a} \tag{VII.14}$$

If the standard compound is benzene and $T_1 = 293$ K Eqs. (VII.13) and (VII.14) can be written as

$$\ln p_2 = \ln p_{sat2} - \beta_a \frac{293}{T_2} \ln \frac{75}{p_1} \quad \text{and} \quad G_2 = G_1 \frac{0.089}{V_2}$$

The most important technological characteristic is the actual product yield or the efficiency of the apparatus which is defined as the ratio of the actual amount G_a of the converted component to the respective amount at equilibrium G_e so that it describes the degree of approach to equilibrium:

$$x_a = \eta = G_a/G_e \tag{VII.15}$$

Calculations of the product yields in heterogeneous processes are more complicated owing to the presence of several phases. The law of conservation of mass makes it possible to calculate the degree of conversion only for one phase. For instance, the degree of conversion (sorption) in adsorption or absorption processes is calculated from the equation

$$x = \frac{G_i^g - G_f^g}{G_i^g} \tag{VII.16}$$

where G_i^g and G_f^g are the initial and final amounts of the converted component in the gas passing through the apparatus.

Eq. (VII.16) is typically approximated by

$$x = \frac{C_i^g - C_f^g}{C_i^g} \tag{VII.17}$$

where C_i^g and C_f^g are the initial and final concentrations (by mass or volume) of the converted component.

Eq. (VII.17) is valid only if the volume (mass) of the transfer phase remains constant. The equation should be modified if the volume (mass) of the transfer phase varies significantly in the course of the process (see Problem 7 in this chapter).

The actual product yield (apparatus efficiency) can be calculated as illustrated below in the case of absorption. Generally, we can write

$$x_a = \eta_{ab} = \frac{C_i^g - C_f^g}{C_i^g - C_g^*} \tag{VII.18}$$

where C_g^* is the concentration of the absorbed component in the gas which is at equilibrium with the mean concentration of the component in the liquid. For instance, in some cases

$$C_g^* = \frac{C_i^{*g} + C_f^{*g}}{2} \qquad \text{(VII.19)}$$

where C_i^{*g} and C_f^{*g} are the concentrations of the absorbed component in the gas which are at equilibrium with its concentrations in the liquid at the entrance and the exit of the apparatus.

Eq. (VII.18) and similar formulas for the apparatus efficiency (for instance, expressed in terms of concentrations in the liquid phase) can be derived from the material balance of the process. The efficiency of desorption is typically calculated in terms of the concentrations in the liquid phase:

$$\eta_d = \frac{C_i^l - C_f^l}{C_l^* - C_f^l} \qquad \text{(VII.20)}$$

The equilibrium concentrations C_g^* and C_l^* can be found in various ways depending on the conditions of the heterogeneous processes.

The apparatus efficiency is calculated from the equilibrium equations though this parameter is determined primarily by the kinetics of the process since the actual amount of the absorbed or desorbed component depends on the mass transfer rate and is, typically, lower than the equilibrium value.

In calculations and simulations of the heterogeneous processes the degree of approach to equilibrium is described by the equilibrium approach criterion

$$\text{Pa} = \frac{1}{1-\eta} \quad \text{or} \quad \text{Pa} = \ln\frac{1}{1-\eta} \qquad \text{(VII.21)}$$

The actual product yield is determined by numerous factors, both chemical ones which affect the chemical reaction rates and the physical and hydrodynamic ones which affect the mass transfer rate.

The form of the overall kinetic equation for the process depends on whether the process is limited by kinetics or diffusion or both, that is, on the ratio of the rate constants of the diffusion and reaction stages. The general equation for the heterogeneous process for the ideal plug flow and incomplete mixing conditions has the following general form:

$$u = dG/d\tau = k\Delta CF \qquad \text{(VII.22)}$$

Under the conditions close to complete mixing Eq. (VII.22) is transformed into

$$u = G/\tau = k\Delta CF \qquad \text{(VII.23)}$$

The concrete forms of the general equations (VII.22) and (VII.23) can be complicated depending on the type of the driving force ΔC, the contact surface F of the phases and the factors affecting the process rate constant k. To make calculations for the reactors and mass-exchange apparatus we have to know, first of all, the process rate constant k which is the most significant characteristic of the apparatus efficiency since it takes into account the complex effects of a variety of independent factors.

For the heterogeneous processes in the two-phase system we can write in the general form

$$k = f(k_1, k_2, k_{side}, \ldots, D_1, D_2, D_1', D_2', \ldots, w_1, w_2, \ldots, \sigma, \nu_1, \nu_2, \rho_1, \rho_2, \ldots, \Gamma_1, \Gamma_2, \Gamma_3, \ldots) \quad \text{(VII.24)}$$

where k_1, k_2, k_{side} are the rate constants for the forward, reverse, and side reactions; D_1, D_2, D_1', D_2' are the diffusion coefficients of the reactants and reaction products; σ is the surface tension at the phase interface; ρ_1 and ρ_2 are the densities of the reactants; ν_1 and ν_2 are the viscosities of the phases; and Γ_1, Γ_2, Γ_3 are the geometric parameters of the apparatus or its main components.

The typical approach is to approximate this complex function by elimination of some factors for the kinetics limited or diffusion limited processes.

The kinetics of the processes involving liquid and gaseous reactants can be illustrated by the absorption (desorption) processes. The overall rates and the apparatus sizes for these processes are typically determined by the physical diffusion stages. The kinetic equations for the diffusion limited process can be written in the following general form:

for absorption $u = k_g F (p - p^*)$; (VII.25)

for desorption $u = k_l F (C^* - C)$ (VII.26)

Here p is the partial pressure of the absorbed component (Pa), p^* is the partial pressure of the absorbed component which is at equilibrium with the liquid (Pa), C is the concentration of the dissolved gas in the liquid (molar fractions), C^* is the concentration of the dissolved gas in the liquid which is at equilibrium with the gas (molar fractions), and k_g and k_l are the mass transfer coefficients expressed in terms of the partial pressure and the concentration in the liquid, respectively.

In calculations of the absorption-desorption processes the equations are, typically, written in terms of appropriate criteria and the mass transfer coefficient is usually calculated. For instance, the following equation can be written:

$$\mathrm{Nu}' = f(\mathrm{Re}, \mathrm{Ga}, \mathrm{Pr}', \Gamma) \quad \text{(VII.27)}$$

Here $Nu' = Kl/D$ is the Nusselt diffusion criterion, $Re = wl/\nu$ is the Reynolds hydrodynamic criterion, $Ga = gl^3/\nu^2$ is the Galileo criterion, $Pr' = \nu/D$ is the Prandtl diffusion criterion, K is the mass transfer coefficient, l is the characteristic linear size, D is the diffusion coefficient, w is the linear velocity of the flow, ν is the kinematic viscosity, Γ is the geometric similarity simplex which characterizes the given apparatus.

The concrete form of Eq. (VII.27) is determined by the parameters of the process and apparatus.

For instance, mass exchange between the surface of an individual bubble, drop or particle and the surrounding phase moving with the relative velocity w_0 is described by the following equation:

$$Nu' = A Re^m (Pr')^n \qquad (VII.28)$$

If the phase interface is inert we have $A \approx 0.6$, $m \approx 1/2$, and $n \approx \approx 1/3$ and if the interface is in free motion $A = 1.1$, $m \approx 1/2$, and $n \approx 1/2$. With increasing turbulence of the system the exponent m increases and the exponent n decreases.

For the pipes with trickling walls we have

$$Nu' = 0.023\, Re^{0.81} (Pr')^{0.44} \qquad (VII.29)$$

For the mass transfer under the turbulence conditions a convenient criterion is the Margulis contact number

$$Ma = k/w \qquad (VII.30)$$

This number characterizes the rate of dissolving of gases in liquids. For instance, under the turbulence conditions of absorption we can say that gases have a good solubility when $Ma > 1$ and a bad solubility when $Ma < 0.1$ and the intermediate solubilities are found in the range $0.1 < Ma < 1$.

The mass transfer in the froth apparatus is described by the following equation:

$$Ma = A Re^m (Pr')^n H_{sp}^p \Gamma^r \qquad (VII.31)$$

Here $H_{sp} = H_f/h_0$ is the specific height of the froth, H_f is the height of the froth, $\Gamma = h_0/d_e$ is the geometric similarity simplex, d_e is the equivalent diameter of the apparatus, and h_0 is the height of the starting liquid layer.

For absorption of gas by liquid under the cross-current conditions we have

$$\eta = \frac{2k_{ab}}{2w_g + k_{ab}} \qquad (VII.32)$$

In calculations of chemisorption processes the driving force or the mass transfer coefficient is usually expressed in terms which take into account the equilibrium conditions and the reaction rate in the liquid phase.

For instance, the equilibrium partial pressure of the absorbed component in a chemisorption process can be written as

$$p^* = \frac{\alpha}{K\psi(1-\alpha)} \qquad \text{(VII.33)}$$

where K is the equilibrium constant of the chemical reaction in the liquid phase, ψ is the Henry's law coefficient, and α is the degree of saturation of the absorbent with the absorbed component. Then we obtain

$$u = k_{ab} F \left(p - \frac{\alpha}{K\psi(1-\alpha)} \right) \qquad \text{(VII.34)}$$

We can write a more accurate equation for the process rate with k_{ab} being independent of the component concentrations in the gaseous and liquid phases if we determine experimentally the driving force of the process as

$$\Delta C = p - p_i^* \qquad \text{(VII.35)}$$

where p_i^* is the equilibrium partial pressure of the absorbed component at the interface under the given hydrodynamic conditions.

Another way to take into account the variation of the chemisorption rate compared with the physical absorption rate is to increase the mass transfer coefficient assuming the driving force to be equal to the driving force of physical absorption. Then we have

$$u = k_l \varkappa F \Delta C \qquad \text{(VII.36)}$$

where $\varkappa$ is the factor for enhancement of absorption in the liquid phase owing to the reaction. This factor is a function of various factors and can be expressed in different ways depending on the model of the chemisorption process. In the general form we can write

$$\varkappa = f(k_1,\ k_2,\ \tau_0,\ p,\ p_i^*,\ C,\ D_1,\ D_2,\ \ldots) \qquad \text{(VII.37)}$$

where τ_0 is the period of renovation (the time of contact between liquid and gas between two successive renovations of the interface).

Calculations of $\varkappa$ proceeding from various process models yield close values. Figures 24 and 25 present the values of $\varkappa$ for some processes. The data of Fig. 24 can be used for the reversible reactions of the first order $A \rightleftarrows B$ in the liquid phase.

The parameter plotted along the horizontal axis in Fig. 24 is

$$\alpha_1 = \frac{1}{k_l} \sqrt{D_A k_1}$$

where k_1 is the rate constant of the first-order reaction (1/s), k_l is the mass transfer coefficient in the liquid phase for physical absorption (m/s), and D_A is the diffusion coefficient of the absorbed gas component (m^2/s).

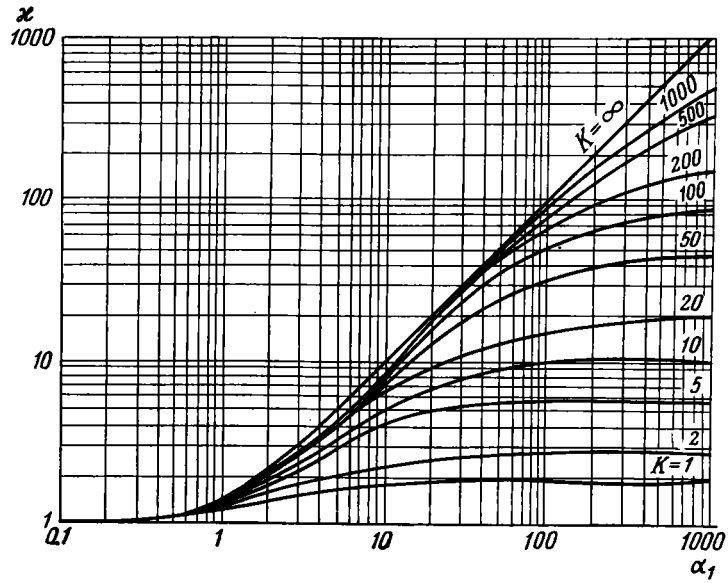


Fig. 24. The factor $\varkappa$ for enhancement of absorption as a function of the equilibrium constant K and the parameter α_1 in the first-order reactions (see the text)

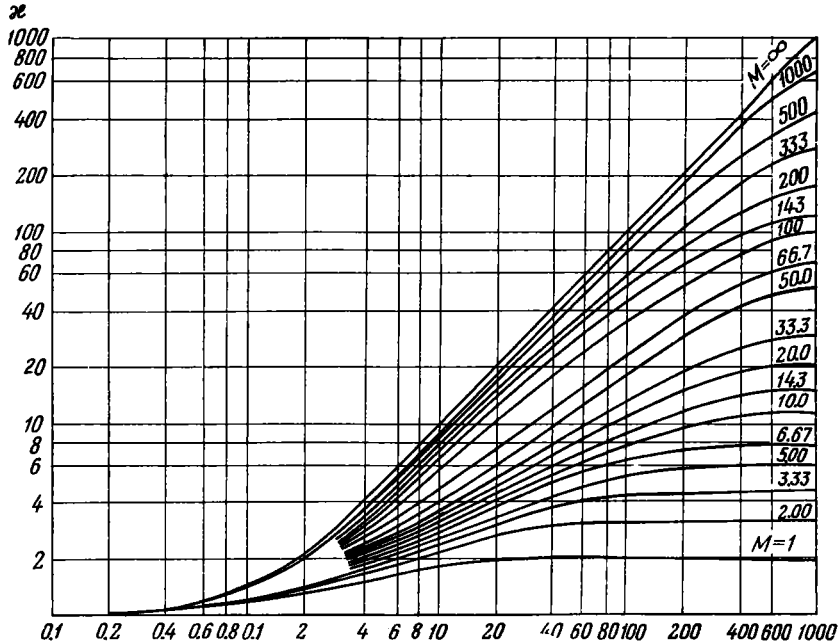


Fig. 25. The factor $\varkappa$ for enhancement of absorption as a function of the parameters M and α_2 in the second-order reactions (see the text).

When the equilibrium constant K is zero, $\varkappa = 1$ and the process is physical absorption. When $K = \infty$ the process is an irreversible reaction.

Figure 25 presents $\varkappa$ as a function of the parameters

$$M = \frac{C_B^l}{nC_A^i} \frac{D_B}{D_A}$$

and

$$\alpha_2 = \frac{1}{k_l} \sqrt{D_A k_2 C_B^l}$$

for the irreversible reaction of the second order between the components A and B. Here k_2 is the rate constant for the second-order reaction (m^3/kmole s), C_B^l is the concentration of the free active component of the absorbent in the bulk of the liquid, C_A^i is the concentration of the component A at the interface, D_A and D_B are the diffusion coefficients of the components, and n is the number of kmoles of B reacting with 1 kmole of A.

There are three regions in Fig. 25 where the solution can be simplified.

(1) The region of small parameters α_2 ($\alpha_2 \leqslant 0.5$) where $\varkappa \approx 1$, that is, where the effect of the reaction on absorption is negligible and the process can be described as physical absorption.

(2) The region of large parameters α_2 compared with M ($\alpha_2 \geqslant 5M$) where $\varkappa$ is independent of α_2 and is equal to $M + 1$ (high-rate reaction).

(3) The region of high parameters M compared with α_2 ($M \geqslant 5\alpha_2$) where $\varkappa$ is independent of M when $\alpha_2 > 2$ and $\varkappa = \alpha_2$.

The area F of the interface is the surface area of the heavier phase (liquid) and is sometimes determined experimentally. When turbulization is high it is difficult to determine F and it is replaced by a theoretical (arbitrary) surface (cross section of the apparatus, the surface of packing, beds, and so on) or volume (reaction volume, volume of the liquid, etc.).

In some cases F can be found from the kinetic equation for the given conditions. For instance, for the continuous-process packed absorption column we obtain for the conditions close to the ideal plug flow

$$F = G_g \int_{p_1}^{p_f} \frac{dp}{u} \qquad \text{(VII.38)}$$

where G_g is the mass flow rate of the absorbed gas (kg/h), p_1 and p_f are the partial pressures of the absorbed gas at the entrance and exit of the column (Pa), and u is the process rate defined as the amount of the gas absorbed by the liquid per unit time per unit area of the

interface between the gas and the liquid (kg/h m^2). Eq. (VII.38) is typically solved by graphical integration.

For the diffusion limited processes the absorption column can be divided into segments in which we can assume u = const and then F can be approximated by

$$F = G_g \Delta p / u_m \tag{VII.39}$$

where Δp is the difference between the partial pressures of the absorbed gas at the entrance and the exit of the segment and u_m is the mean process rate.

The rate of dissolving in the L-S system decreases with increasing concentration C of the dissolved component in the liquid according to the kinetic equation of physical dissolving

$$u = kF\,(C_{sat} - C) \tag{VII.40}$$

where C_{sat} is the saturation concentration and k is the rate constant of physical dissolving which depends on the rates of diffusion and disintegration of the crystalline lattice.

The rate constant of physical dissolving is sometimes written as

$$k = D/\delta \tag{VII.41}$$

where D is the diffusion coefficient of the dissolved component and δ is the theoretical thickness of the boundary diffusion layer.

The rate of physical dissolving can be expressed in terms of the following criteria:

$$\mathrm{Nu'} = f\,(\mathrm{Re},\ \mathrm{Pr'},\ \mathrm{Ar}) \tag{VII.42}$$

For instance, Eq. (VII.42) for dissolving of the suspended salt crystals under the conditions of forced convection (Re = const) has the following form:

$$\frac{kl}{D} = A\left(\frac{\nu}{D} \cdot \frac{gl^3}{\nu^2} \cdot \frac{\rho_s - \rho_l}{\rho_l}\right)^{1/3} \tag{VII.43}$$

Here l is the mean linear size of the crystal, ρ_s and ρ_l are the densities of the solid and the liquid (solvent) and A is a constant.

For the reactors with agitators the mass-transfer coefficient k (in kmole/m^{2}h) is given by equation

$$\frac{kd}{D} = A\left(\frac{\nu}{D}\right)^{-0.5} B\frac{nd^2}{\nu} \tag{VII.44}$$

where A and B are the parameters describing the agitator (for instance, for the propeller agitator $A = 0.13$ and $B = 0.58$) and n is the rotation rate of the agitator (1/s).

The rate of chemical dissolving can be described by Eq. (VII.40) where the coefficient k takes into account the effects of the chemical and physico-chemical factors. More complicated kinetic equations for specific processes can be found in literature.

Calculations of the Mass-transfer Processes and Reactors for the L-G Systems

Problem 1. Find the volume of oxygen from the air which will be dissolved in 100 kg of water at the temperature 18°C under the pressure 1×10^6 Pa.

Solution. According to Henry's law we have

$$N_g = \psi p \qquad \text{(VII.45)}$$

where N_g is the molar fraction of the gas in solution, ψ is the Henry's

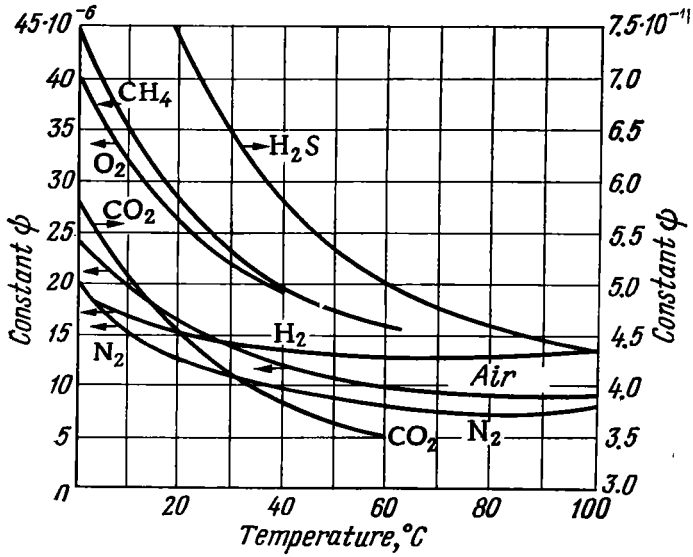


Fig. 26. The Henry's law constant ψ for several gases and water as a function of temperature.

law constant for the given system, and p is the partial pressure of the gas over the liquid.

As a rule the constant ψ decreases with increasing temperature. The constant ψ depends on the natures of the gas and the liquid, and Fig. 26 presents values of ψ for some gases and water. If the gas pressure over the solution is 10^5 Pa the constant ψ is equal to the molar fraction of the gas in solution ($\psi = N_g$).

From Fig. 26 we see that for oxygen at 18 °C $\psi = 26 \times 10^{-6}$. The partial pressure of oxygen in the air at the pressure 1×10^6 Pa is 0.21×10^6 Pa. The molar fraction of oxygen in solution is $NO_2 = 26 \times 10^{-6} \times 10 \times 0.21 = 54.6 \times 10^{-6}$, that is, 1 kmole of water contains 54.6×10^{-6} kmole of oxygen. Hence, the amount of oxygen dissolved in 100 kg of water is $100 \times 54.6 \times 10^{-6}/18$ kmole $= 6.71 \times 10^{-3}$ m³.

Problem 2. A mixture of 30% benzene, 45% toluene, and 25% *o*-xylene is heated to 100 °C.

Calculate the equilibrium composition of the vapour over the liquid. The vapour pressures at 100 °C for the components: benzene—1.78×10^5 Pa (1340 mm Hg), toluene—0.75×10^5 Pa (560 mm Hg), *o*-xylene—0.29×10^5 Pa (210 mm Hg).

Solution. According to the Raoult law the partial pressure of the component A in the vapour is

$$p_A = N_{A_l} p_0 \qquad \text{(VII.46)}$$

where N_{A_l} is the molar fraction of the component A in the solution and p_0 is the vapour pressure of the pure component A.

Calculations will be made for 100 kg of the mixture which contain 30/78 = 0.384 kmole of benzene, 45/92 = 0.490 kmole of toluene and 25/106 = 0.236 kmole of *o*-xylene. The total is 1.110 kmoles.

Hence, the mixture contains 0.384/1.11 = 34.6 mol. % of benzene, 0.49/1.11 = 44.1 mol. % of toluene, and 0.236/1.11 = 21.3 mol. % of *o*-xylene.

The partial pressure of each component in the vapour is given by Eq. (VII.46): $p_{benz} = 0.346 \times 1340 \times 133.3 = 0.618 \times 10^5$ Pa, $p_{tol} = 0.441 \times 560 \times 133.3 = 0.33 \times 10^5$ Pa, and $p_{xyl} = 0.213 \times 210 \times 133.3 = 0.059 \times 10^5$ Pa, so that the total vapour pressure is 1.007×10^5 Pa (at 100 °C).

Hence, the vapour contains $0.618 \times 10^5 \times 100/1.007 \times 10^5 = 61.3$ % of benzene, $0.33 \times 10^5 \times 100/1.007 \times 10^5 = 32.8$ % of toluene, and $0.059 \times 10^5 \times 100/1.007 \times 10^5 = 5.9$% of *o*-xylene.

Problem 3. At 20 °C the pressure of the water vapour is 2340 Pa. Calculate the vapour pressure over the water containing 15 % (by mass) of glycerol.

Solution. The Raoult law yields

$$\frac{p_0 - p}{p_0} = \frac{n}{n_{solv} + n} \qquad \text{(VII.47)}$$

where p_0 is the vapour pressure for the pure solvent, p is the pressure of the solvent vapour over solution of a given concentration, n is the number of moles of the dissolved component in the solution, and n_{solv} is the number of moles of the solvent in the solution.

Molecular masses: water—18, glycerol—92. The molar fraction of glycerol in the solution is

$$\frac{n_{gl}}{n_{water}+n_{gl}}=\frac{0.15/92}{0.85/18+0.15/92}=0.0332$$

Eq. (VII.47) yields $(2340-p)/2340 = 0.0332$. Hence, the vapour pressure over the 15% glycerol solution in water at 20 °C is $p = 2262$ Pa (17 mm Hg).

Problem 4. The vapour pressure p_0 of pure ethanol at 20 °C is 5925 Pa and that of methanol is 11 860 Pa.

Calculate the composition (in % by mass) of the vapour over the mixture of equal amounts (by mass) of ethanol and methanol.

Solution. Consider the mixture of 1 g of ethanol and 1 g of methanol. The results of calculations are given in the table below.

	Ethanol	Methanol
Amount	1	1
Molecular mass M_i	46	32
Number of moles in mixture	1/46	1/32
Molar fraction in mixture $N_i=\frac{1/M_i}{1/M_1+1/M_2}$	0.410	0.590
Partial pressure over mixture $p_i=N_ip_0$, Pa	$0.410\times 5925=2430$	$0.590\times 4860=7000$
Molar fraction in vapour $N_i'=p_i/\sum p_i$	$\frac{2430}{2430+7000}=0.258$	$\frac{7000}{2430+7000}=0.742$

Hence, the vapour contains 25.8 mol.% of ethanol and 74.2 mol.% of methanol. Let us express the results in percentages by mass. If the mass of ethanol in 100 g of vapour is g_1 then the mass of methanol in 100 g of vapour is $g_2 = 100 - g_1$. Then the molar fraction of ethanol in the vapour is

$$N_1'=\frac{g_1/46}{\frac{g_1}{46}+\frac{100-g_1}{32}}$$

and the molar fraction of methanol is

$$N_2'=\frac{\frac{100-g_1}{32}}{\frac{g_1}{46}+\frac{100-g_1}{32}}$$

Using the values of N_1' and N_2' given in the table above we obtain $g_1 = 33.3\%$ and $g_2 = 66.7\%$.

Problem 5. Calculate the driving force for absorption of ammonia by water under the following conditions: (a) parallel flows of the gas and liquid, (b) counterflow, and (c) complete mixing. Absorption is carried out under the pressure of 0.1×10^6 Pa and at the temperature of 27 °C. The initial concentration of ammonia in the gas is

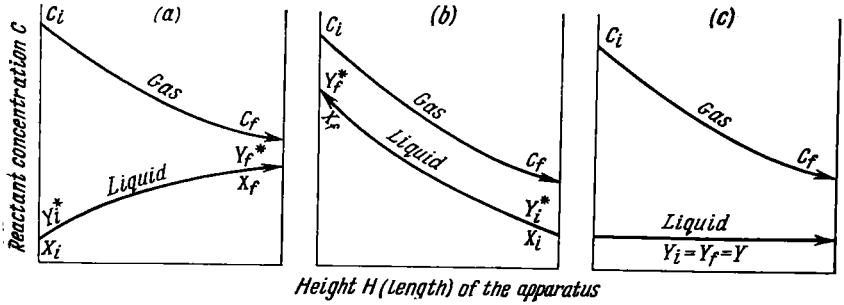


Fig. 27. Variation of the reactant concentrations for parallel flows (a), for counterflow (b), and for complete mixing of the liquid (c).

$C_1 = 4$ % (by volume) and in water $X_1 = 0.05$ kmole/m³ and the final concentration of ammonia is $C_f = 0.8\%$ (by volume) in the gas and $X_f = 0.25$ kmole/m³ in water.

Solution. The mean driving force of a process can generally be written as

$$\Delta C_m = \frac{\Delta C_1 - \Delta C_f}{2.3 \log \frac{\Delta C_1}{\Delta C_f}} \qquad \text{(VII.48)}$$

The local driving forces ΔC_i and ΔC_f depend on the directions of the flows (Fig. 27).

(a) For parallel flows we have

$$\Delta C_{m\downarrow\downarrow} = \frac{(C_1 - C_1^*) - (C_f - C_f^*)}{2.3 \log \frac{C_1 - C_1^*}{C_f - C_f^*}}$$

(b) For counterflow we have

$$\Delta C_{m\downarrow\uparrow} = \frac{(C_1 - C_f^*) - (C_f - C_1^*)}{2.3 \log \frac{C_1 - C_f^*}{C_f - C_1^*}}$$

(c) For complete mixing we have

$$\Delta C_m^{mix} = \frac{(C_1 - C^*) - (C_f - C^*)}{2.3 \log \frac{C_1 - C^*}{C_f - C^*}}$$

The asterisk in the above equations denotes the equilibrium pressures of ammonia over the solution in a given part of the apparatus.

The constant of the phase equilibrium (the Henry's law coefficient) between ammonia and its aqueous solutions (up to the concentration of 3 kmole/m^3) can be found from the following empirical equation:

$$\log \psi = 9.705 - 1922/T \qquad \text{(VII.49)}$$

Here ψ is expressed in terms of m^3 Pa/kmole and T is the absolute temperature.

For 300 K Eq. (VII.49) yields $\psi = 2 \times 10^3$. The respective equilibrium pressures of ammonia are $C_i^* = 0.05 \times 2 \times 10^3 = 100$ Pa and $C_f^* = 0.25 \times 2 \times 10^3 = 500$ Pa.

The actual concentrations of ammonia are $C_i = 10^5 \times 0.04 = 4000$ Pa and $C_f = 10^5 \times 0.008 = 800$ Pa.

The above equations yield the following driving force values: (a) $\Delta C_{m\downarrow\downarrow} = 1400$ Pa; (b) $\Delta C_{m\downarrow\uparrow} = 1700$ Pa; and (c) $\Delta C_m^{mix} = 1300$ Pa. It can be seen that under the given conditions the counterflow process provides for the minimum "path length".

Problem 6. Using the conditions specified in Problem 5 calculate the driving force of the process in the apparatus with cross current flows.

Solution. The driving force of the process in the apparatus with the cross current flows, for instance in the froth absorber, can be calculated by the following formula which is sufficiently accurate for technological calculations:

$$\Delta C_{cross} = \frac{(C_l - C_i^*) - (C_l - C_f^*)}{2.3 \log \dfrac{C_l - C_i^*}{C_l - C_f^*}} - \frac{C_l - C_f}{2} \qquad \text{(VII.50)}$$

Using the results obtained in Problem 5 we find $\Delta C_m^{cross} = 2100$ Pa. As the driving force under the counterflow conditions was found to be 1700 Pa we see that the cross-current process is more efficient by $(2100-1700) \times 100/2100 \approx 20\%$.

Problem 7. Calculate the degree of conversion (the degree of sorption) for the absorption (adsorption) process if the initial and final concentrations (by volume) of the processed component are C_i and C_f.

Solution. The degree of sorption is given by Eq. (VII.16):

$$x = \frac{G_i - G_f}{G_i} \times 100\%$$

Here G_i and G_f are the initial and final amounts of the processed component. This equation is, typically, reduced to Eq. (VII.17)

$$x = \frac{C_i - C_f}{C_i} \times 100\%$$

where C_1 and C_f are the initial and final concentrations per unit volume (by volume or by mass) of the processed component. This equation is valid only if the volume of the absorbing phase is constant. If the volume varies in the process this variation should be taken into account.

Let us derive a formula for the absorbing phase with varying volume. The initial and final volumes of the absorbing phase are V_1 and V_f and the initial and final percentage concentrations of the processed component are C_1 and C_f. Then the degree of sorption is

$$x = \frac{\frac{C_1V_1}{100} - \frac{C_fV_f}{100}}{\frac{C_1V_1}{100}} \times 100\%$$

Since the initial and final volumes are not known let us express V_f is terms of V_1. If we ignore the effect of volume variation on the amount of absorbed component we can write

$$V_f = V_1 - \frac{(C_1 - C_f)\,V_1}{100}$$

Then we obtain

$$x = \frac{\frac{C_1V_1}{100} - \frac{C_f\left[V_1 - \frac{(C_1-C_f)\,V_1}{100}\right]}{100}}{\frac{C_1V_1}{100}} \times 100\% = \frac{C_1 - C_f\left(1 - \frac{C_1-C_f}{100}\right)}{C_1} \times 100\% \qquad \text{(VII.51)}$$

More accurate calculations yield

$$x = \frac{\frac{C_1V_1}{100} - \frac{C_f\left(V_1 - \frac{C_1V_1}{100}\right)}{100}}{\frac{C_1V_1}{100}} \times 100\%$$

and

$$x = \frac{C_1 - C_f}{C_1\left(1 - \frac{C_f}{100}\right)} \times 100\% \qquad \text{(VII.52)}$$

Both equations yield practically identical results.

Let us take $C_1 = 50\%$ (by volume) and $C_f = 5\%$ (by volume), that is, the change of gas volume owing to sorption is considerable. Eq. (VII.51) yields $x = 94.5\%$ and Eq. (VII.52) also yields $x = 94.5\%$. At the same time the value of x found from Eq. (VII.17) is 90%, that is, Eq. (VII.17) gives a considerable error which decreases with decreasing difference between C_1 and C_f.

Problem 8. Calculate the diffusion coefficient of ammonia in the air at 25 °C and 10^5 Pa.

Solution. The diffusion coefficient D of a gas A in the gas B (in m^2/s) can be found from the following semiempirical formula:

$$D = \frac{0.00435 \times 10^{-4} T^{3/2}}{P\,(v_A^{1/3} + v^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \qquad \text{(VII.53)}$$

Here T is the absolute temperature K, P is the total pressure (10^5 Pa), v_A and v_B are the molar volumes of the gases A and B (cm^3/mole), and M_A and M_B are the molecular masses of A and B.

The molar volumes are determined as the sums of atomic volumes of the elements comprising the gas (see Appendix I). For instance for the vapour of benzene C_6H_6 we obtain

$$v_{benz} = 6 \times 14.8 + 63.7 - 15 = 96 \text{ cm}^3\text{/mole}$$

The diffusion coefficient can also be found from other, more complicated formulas, for instance, from the following very accurate formula:

$$D = \frac{0.151 \times 10^{-4} \left(\frac{T}{100}\right)^{1.81} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{P\left[\left(\frac{v_A}{100}\right)^{0.4} + \left(\frac{v_B}{100}\right)^{0.4}\right]^2 \left(\frac{T_A^{cr} T_B^{cr}}{10\,000}\right)^{0.14}} \qquad \text{(VII.54)}$$

Here T_A^{cr} and T_B^{cr} are the critical temperatures of the gases A and B.

Appendix II presents the diffusion coefficient values D_0 for some gases at $p_0 = 10^5$ Pa and $T_0 = 273$ K.

The diffusion coefficient D at the temperature T and pressure P can be found from D_0:

$$D = D_0 \frac{p_0}{P} \left(\frac{T}{T_0}\right)^{3/2} \qquad \text{(VII.55)}$$

For ammonia we have $M_A = 17$, $v_A = 15.6 + 3 \times 3.7 = 26.7$ cm^3/mole, $T_A^{cr} = 405$ K and for the air we have $M_B = 29$, $v_B = 29.9$ cm^3/mole, and $T_B^{cr} = 132$ K.

Eq. (VII.53) yields $D = 0.185 \times 10^{-4}$ m^2/s and Eq. (VII.54) yields $D = 0.180 \times 10^{-4}$ m^2/s, that is, the results are practically identical.

Problem 9. Calculate the diffusion coefficient (in m^2/s) of ammonia in water at 25 °C.

Solution. The diffusion coefficient of a gas A in the solvent B at 20 °C is given by the following formula:

$$D_{20} = \frac{10^{-6}}{ab\sqrt{\mu_{20}}\,(v_A^{1/3} + v_B^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \qquad \text{(VII.56)}$$

Here μ_{20} is the viscosity of the solvent at 20 °C (10^6 Pa s), a and b are the factors describing the gas and the solvent: for gases $a = 1$, for water $b = 4.7$, for methanol and ethanol $b = 2$, and for acetone $b = 1.15$.

The temperature dependence of the diffusion coefficient of gases in liquids is described by the following equation:

$$D = D_{20}\left[1 + \frac{0.20\sqrt{\mu_{20}}}{\rho^{1/3}}(t - 20)\right] \qquad \text{(VII.57)}$$

Here ρ is the density of the solvent (kg/m^3).

The following simple formula has been found valid for many systems:

$$D = \frac{7.4 \times 10^{-12}(dM_B)^{1/2}}{\mu v_A^{0.6}} \qquad \text{(VII.58)}$$

For diethyl ether, benzene, and heptane $d = 1$; for water $d = 2.6$; for methanol $d = 1.9$; and for ethanol $d = 1.5$.

Let us first find the diffusion coefficient for ammonia in water at 20 °C. We have (see Problem 8) $a = 1$, $b = 4.7$, $\mu = 10^6$ Pa s, $v_A = 26.7$, $v_B = 2 \times 3.7 + 7.4 = 14.8$, $M_A = 17$, $M_B = 18$.

Then Eq. (VII.56) yields $D_{20} = 0.244 \times 10^{-8}$ m^2/s. Hence, the diffusion coefficient of ammonia in water ($\rho = 1000$ kg/m^3) at 25 °C is given by Eq. (VII.57): $D = 0.27 \times 10^{-8}$ m^2/s.

To compare, Eq. (VII.58) where $d = 2.6$ and $\mu_{25} = 0.9 \times 10^6$ Pa s yields $D = 0.25 \times 10^{-8}$ m^2/s, that is, a similar value.

Problem 10. Calculate the coefficient of effective diffusion (the coefficient of mixing) for absorption of ammonia by water in the froth apparatus at 20 °C. The velocity of gas in the apparatus is 2 m/s, the flow rate of the liquid is 5 m^3/m^2 h, the starting height of the liquid layer is 20 mm.

Solution. The coefficient of mixing in the froth apparatus is given by equation

$$\varepsilon_m = 0.1 w^{1.15} H_f \qquad \text{(VII.59)}$$

where ε_m is the coefficient of mixing (m^2/h), w_l is the flow rate of the liquid (m^3/m^2 h), and H_f is the height of the froth layer (m).

The height of the froth layer can be found by the following equation:

$$H_f = 4.35 \times 10^{-5} \frac{h_0^{0.6} w_g^{0.5}}{\sigma^{1.3} \nu_l^{0.25}} \qquad \text{(VII.60)}$$

Here h_0 is the starting height of the liquid layer (m), w_g is the velocity of the gas (m/s), σ is the surface tension of the liquid (kg/m) and ν is the kinematic viscosity of the liquid (m^2/s).

For the air-water system and for similar systems at the room temperature Eq. (VII.60) can be simplified:

$$H_f = 0.806 h_0^{0.6} w_g^{0.5} \qquad \text{(VII.61)}$$

Hence, we obtain for the above conditions $H_f = 0.11$ m and $\varepsilon_m = 7 \times 10^{-2}$ m²/h $= 0.195 \times 10^{-4}$ m²/s.

The comparison with the results found in Problem 9 shows that the parameter ε_m which describes mass transfer by turbulent liquid

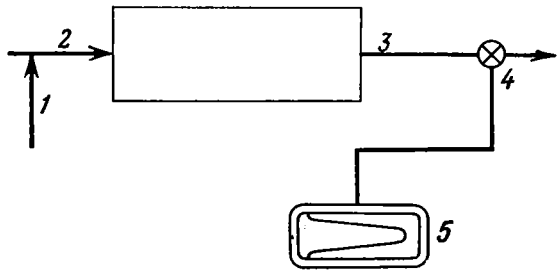


Fig. 28. Diagram describing measurement of indicator concentrations
1—input of indicator; *2*—entry to the apparatus; *3*—exit from the apparatus; *4*—concentration detector; *5*—recorder.

flow is larger by about four orders of magnitude than the coefficient of molecular diffusion in the same system.

Problem 11. (see [18], p. 52). Calculate the mean time of residence of the reactants in the reactor proceeding from the concentrations of an indicator measured at the outlet of the reactor at given periods. The measurement results:

τ, c	0	10	20	30	40	50	60	70	80	90	100
C, μ mole/litre	0	0	1	4	11	10	7	4	2	0.5	0

Solution. The mean time of residence of the reactant increases with increasing reactor volume v_r and decreases with increasing flow rate V of the reactant. We can derive a formula similar to Eq. (VI. 11):

$$\tau_m = V/v_r$$

The time of residence of a particle is a random variable.

If we introduce at a given moment an indicator into the reactor and monitor its concentration C we can use the following formula of the probability theory for calculating τ_m (see Fig. 28):

$$\tau_m = \frac{\int_0^\infty \tau C(\tau)\, d\tau}{\int_0^\infty C(\tau)\, d\tau} \qquad \text{(VII.62)}$$

The integral in the denominator of Eq. (VII.62) is the normalization factor. Since the experimental results given above show that $C = 0$ for $\tau > 100$ s (no indicator left in the reactor) then for any function $\varphi(\tau)$ which contains C as a factor we can write

$$\int_0^{\infty} \varphi(\tau)\, d\tau = \int_0^{100} \varphi(\tau)\, d\tau$$

The integrals can be approximated by the formula of rectangles:

$$\int_a^b \varphi\, d\tau \approx \Delta\tau\,(\varphi_1 + \varphi_2 + \varphi_3 + \ldots + \varphi_{n-1}) \qquad \text{(VII.63)}$$

Here $\Delta\tau$ is the interval between successive values of τ which is assumed to be constant (in our case $\Delta\tau = 10$ s), and φ_1, φ_2, etc. are the successive values of the function. The last value φ_n is not taken into account and the formula ends with φ_{n-1}.

As Eq. (VII.62) contains C both in the denominator and the numerator the dimension of C is irrelevant.

Preliminary calculations yield the following results:

τ	0	10	20	30	40	50	60	70	80	90	100
C	0	0	1	4	11	10	7	4	2	0.5	0
τC	0	0	20	120	440	500	420	280	160	45	0

Then we find from Eq. (VII.63): $\tau_m = 50$ s.

Problem 12. (see [18]). Calculate the degree of conversion for the irreversible reaction of the first order with the reaction constant $k = 0.1$ s^{-1} from the distribution of the residence times for particles using the results obtained in Problem 11.

Solution. It should be noted that the results obtained for the irreversible reaction of the first order may also be applied to the reversible reactions of the first order. Furthermore, the equations of heat and mass transfer are similar to the equation for the reversible reaction of the first order (and the equation for absorption when the equilibrium pressure of the absorbed component is zero is similar to the equation for the irreversible reaction of the first order).

The reaction rate is

$$u = k(C_A - C_A^*)$$

where C_A^* is the equilibrium concentration of the component A.

The rate of absorption per unit surface area is

$$u_{ab} = K_M(C_A - C_A^{*1}) \qquad \text{(VII.64)}$$

where K_M is the mass transfer coefficient.

The heat flow (see Chapter III) is described by

$$Q_h = K_h\,(T_1 - T_2)$$

where K_h is the heat transfer coefficient, and T_1 and T_2 are the temperatures.

Hence, the results obtained for the first-order reactions can largely be applied (taking into account the phase motion) to the mass- and heat-transfer processes.

The irreversible reaction of the first order is described by the following kinetic equation:

$$dC_A/d\tau = -kC_A$$

Hence we obtain

$$C_A = C_A^0 \exp(-k\tau) \qquad \text{(VII.65)}$$

where C_A^0 is the initial concentration of the component A.

Under the isochoric conditions the degree of conversion is

$$x = 1 - C_A/C_A^0 \qquad \text{(VII.66)}$$

In Eq. (VII.65) τ is the time of reaction which is often replaced by the mean residence time. However, this approach in the general case can be incorrect.

To obtain the correct result we should use the distribution of the residence time with the same normalization factor as in Eq. (VII.62):

$$x = 1 - \frac{\int_0^\infty e^{-k\tau} C\, d\tau}{\int_0^\infty C\, d\tau} \qquad \text{(VII.67)}$$

Using the approximated Eq. (VII.63) let us calculate the degree of conversion from Eq. (VII.67). The preliminary data for integration are:

τ	0	10	20	30	40	50	60	70	80	90	100
C	0	0	1	4	11	10	7	4	2	0.5	0
$e^{-k\tau}$	—	—	0.135	0.0498	0.0183	0.0067	0.0025	0.0009	0.0003	0.0001	—
$e^{-k\tau}C$	0	0	0.135	0.198	0 202	0.067	0.017	0.004	0.001	0.000	0

Eqs. (VII.63) and (VII.67) yield $x = 0.984$.

Problem 13. Calculate the consumption of sulphuric acid for drying the air in the apparatus producing 1000 m³/h of dry air. The initial concentration of moisture in the air is $Y_1 = 0.02$ kg per 1 kg of dry air and the final concentration is $Y_f = 0.006$ kg of moisture per 1 kg of dry air. The initial content of water in the acid is $X_1 = 0.75$ kg per 1 kg of monohydrate and the final content of water in the acid is $X_f = 1.0$ kg per 1 kg of monohydrate. Absorption of water is carried out at the atmospheric pressure.

Solution. The consumption of sulphuric acid (monohydrate) per 1 kg of dry air is

$$L = G\,(Y_1 - Y_f)/(X_f - X_1) = 0.015 \text{ kg}$$

As the density of the dry air is 1.29 kg/m³ the total consumption of sulphuric acid is $1000 \times 1.29 \times 0.015 = 19.4$ kg/h.

Problem 14. ([26], p. 407). The absorbing packing for absorption of the acetone vapour from the air is irrigated with 3000 kg of water per 1 hour. The water temperature is 20 °C. The air contains 6% (by volume) of acetone. The flow rate of pure air through the absorber is 1400 m³/h. The degree of absorption of the acetone vapour is 98%.

Calculate the height of the absorption column with $25 \times 25 \times 3$ mm ceramic packing rings. The mass transfer coefficient for acetone is $K_g = 0.4$ kmole/m² h per unit concentration difference in the gaseous phase (kmoles of acetone per 1 kmole of the air). The gas velocity is assumed to be 25% lower than the velocity corresponding to the beginning of emulsification of the liquid. The equilibrium concentrations in the acetone-water system are reported in literature.

Solution. The amount of acetone absorbed by water per 1 hour is

$$G_{ab} = 1400 \times 0.06 \times 0.98/(1 - 0.06)\,22.4 = 3.9 \text{ kmoles}$$

The initial concentration of acetone in the absorbing water (at the top of the column) is $X_t = 0$. The final concentration of acetone in the water discharged from the column (at the bottom of the column) is $X_b = G_{ab}/L = 3.9 \times 18/3000 = 0.0234$ kmole per 1 kmole of water (L is the water flow rate).

The initial concentration of acetone in the air (at the bottom of the column) is $Y_b = 0.06/0.94 = 0.0639$ kmole per 1 kmole of the air. The concentration of acetone in the air discharged from the column (at the top of the column) is $Y_t = 3.9 \times 0.02 \times 22.4/0.98 \times 1400 = 0.00128$ kmole per 1 kmole of the air.

Figure 29 presents the plot of the process passing through these points and the equilibrium plot described by the equation $Y^* = 1.68X$.

The driving force of absorption at the bottom of the column is

$$\Delta Y_b = Y_b - Y_b^* = 0.0639 - 0.0393 =$$
$$= 0.0246 \text{ kmole of acetone/1 kmole of air}$$

The value of Y_b^* is found from the equation of the equilibrium curve for X_b:

$$\Delta Y_b = 1.68 \times 0.0234 = 0.0393 \text{ kmole of acetone/kmole of air}$$

The driving force of absorption at the top of the column is

$$\Delta Y_t = Y_t - Y_t^* = 0.00128 - 0 =$$
$$= 0.00128 \text{ kmole of acetone/1 kmole of air}$$

The mean driving force of the process is $\Delta Y_m = (0.0246 - 0.00128)/2.3\log(0.0246/0.00128) = 0.0079$ kmole of acetone per 1 kmole of the air.

The surface area of mass transfer is

$$F = G_{ab}/K_g \Delta Y_m = 1230 \text{ m}^2$$

The volume of the layer of ceramic rings which provides for a given mass-transfer surface area in the packing column under the liquid film conditions is given by the following equation:

$$F = H_p S \sigma_p \psi_w \qquad \text{(VII.68)}$$

Here $H_p S = v$ is the volume of packing (m^3), H_p is the height of the packing layer (m), $S = \pi D^2/4$ is the cross-section area of the column (m^2), D is the column diameter (m), σ_p is the specific surface area of the packing (m^2/m^3), and ψ_w is the coefficient of wetting of the packing (for the irrigation density $L_0 > 5$ m^3/m^2 h it is usually assumed that $\psi_w = 1$). Hence we obtain

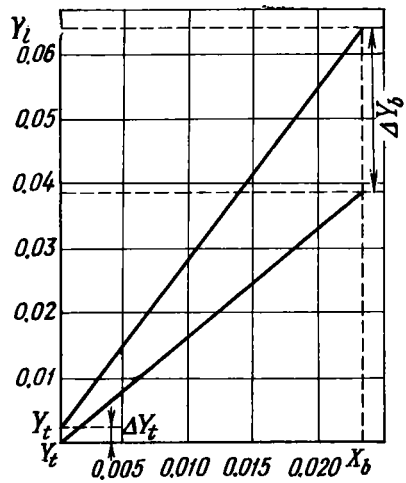


Fig. 29. The equilibrium and partial pressures in the gas phase as a function of the concentration of the liquid phase (Problem 14).

$$v = 1230/204 \times 1 = 6 \text{ m}^3$$

(the specific surface area of the ring packing is 204 m^2/m^3, see Appendix III).

The gas velocity w_g corresponding to the beginning of emulsification is found from the following equation:

$$\log\left[\frac{w_g^2 \sigma_p \rho_g \mu_l^{0.16}}{0.00145 g v_f^3 (\rho_l - \rho_g)}\right] = A - 1.75\left(\frac{L}{G}\right)^{0.25}\left(\frac{\rho_g}{\rho_l - \rho_g}\right)^{0.125} \qquad \text{(VII.69)}$$

Here v_f is the free volume of the packing (m^3/m^3), ρ_g and ρ_l are the densities of the gas and the liquid (kg/m^3), μ_l is the viscosity of the

liquid (Pa s), A = — 0.125 for the rectification process and A = = 0.022 for the absorption process, L is the flow rate of the liquid (kg/h), and G is the flow rate of the gas (kg/h). For our process conditions we have $L = 3000$ kg/h, $\rho_g = 1.2$ kg/m³, $G = 1400 \times 1.29 + 3.9 \times 58/2 \approx 1900$ kg/h, $\rho_l = 1000$ kg/m³, $L/G = 1.58$, $\rho_g/\rho_l = 0.0012$, $\mu_l = 10^{-3}$ Pa s, $v_f = 0.74$ m³/m³ (see Appendix III).

Substituting the above data in Eq. (VII.69) we find $w_g = 1.56$ m/s. The actual gas velocity is taken to be 25% less, that is, $w_g = 1.56 - 0.25 \times 1.56 = 1.17$ m/s.

The cross-section area of the column is

$$S = 1400 \times 293/3600 \times 273 \times 1.17 = 0.356 \text{ m}^2$$

Hence, the column diameter is $D = 0.67$ m. The height of the packing layer is

$$H_p = v/S = 16.9 \text{ m}$$

The irrigation density is

$$L_0 = L/\rho_l S = 8.4 \text{ m}^3/\text{m}^2\text{h}$$

For such irrigation density $\psi_w = 1$ as assumed above.

Problem 15 (see [26]). Pure water is used to absorb 1 ton/h of SO_2 from the roaster gas containing 5% (by volume) of SO_2. The degree of absorption of SO_2 is 90%. The consumption of water is assumed to be 20% higher than the minimum necessary amount. The overall pressure is 10^5 Pa. The temperature of the absorbing water is 20 °C.

Calculate the driving force of the process.

Solution. The parameters of the SO_2-water systems at 20 °C:

Mass parts of SO_2 per 100 mass parts of H_2O	1	0.7	0.5	0.3	0.2	0.1	0.05	0.02
Partial pressure of SO_2 over solution, Pa	7850	5200	3460	1880	1120	426	160	66.7

The partial pressure of SO_2 in the starting gas at the bottom of the absorber is $p_b = 0.05 \times 10^5 = 5000$ Pa. This pressure corresponds to the SO_2 concentration of 0.69 kg per 100 kg of water (at equilibrium).

The total amount of absorbed SO_2 is 1000 kg/h. Thus, the minimum amount of the absorbing water is

$$L_{min} = 1000 \times 100/0.69 = 145\,000 \text{ kg/h or } 145 \text{ m}^3/\text{h}$$

The actual consumption of water is $L = 145 \times 1.2 = 174$ m³/h.

The driving force of the absorption process at the top of the absorber is

$$\Delta p_t = p_t - p_t^*$$

The SO_2 concentration in the gas discharged from the absorber (at the top of the apparatus) is

$$C_t = 5\,(1 - 0.9) \times 100/(95 + 5\,(1 - 0.9)) = 0.52\%$$

Hence we obtain

$$p_t = 10^5 \times 0.0052 = 520 \text{ Pa}$$

Since the water fed to the absorber is pure $p_t^* = 0$ and $\Delta p_t = 520$ Pa.

The driving force of the absorption process at the bottom of the absorber is

$$\Delta p_b = p_b - p_b^*$$

As calculated above $p_b = 5000$ Pa. The water discharged from the absorber (at the bottom) contains $X_b = 1000 \times 100/174\,000 = 0.575$ kg of SO_2 per 100 kg of water. This SO_2 concentration in solution (at equilibrium) corresponds to the partial pressure of SO_2 of 4100 Pa over the solution. Hence we obtain $\Delta p_b = 900$ Pa. Assuming that the equilibrium curve is a straight line we can calculate the mean driving force for the process:

$$\Delta p_m = (900 + 520)/2 = 710 \text{ Pa}.$$

Problem 16. (see [26]). Calculate the mass transfer coefficient k_M from the results of Problem 15. The gas velocity is 0.35 m/s, absorption occurs under the liquid film conditions on coke lumps with the mean size of 75 mm. The specific surface area of the packing is $\sigma_p = 41.7$ m^2/m^3 and the free volume of the packing is $v_f = 0.58$ m^3/m^3.

Solution. In this case the diffusion resistance of the liquid is negligible compared to the resistance of the gas so that the overall coefficient k_M of mass transfer is approximately equal to the mass transfer coefficient k_g for the gas. Then we can make use of the equation for the liquid film conditions of the absorption process similar to Eq. (VII.28).

$$\text{Nu}'_g = 0.027\text{Re}_g^{0.8}\,(\text{Pr}'_g)^{0.33} \qquad \text{(VII.70)}$$

Here $\text{Nu}'_g = k_g d_e p_{1.g}/\rho_g D_g$ is the Nusselt diffusion criterion, $\text{Re}'_g = 4w_g\rho_g/\sigma_p\mu_g$ is the Reynolds criterion and $\text{Pr}'_g = 3600\,\mu_g/\rho_g D_g$ is the Prandtl diffusion criterion for the gas, k_g is the mass transfer coefficient for the gas (kmole/m^2 h 10^6 Pa), $d_e = 4v_f/\sigma_p$ is the equivalent diameter of the packing lumps (m), v_f is the free volume of the packing (m^3/m^3), σ_p is the specific surface area of the packing (m^2/m^3), ρ_g is the gas density (kg/m^3), μ_g is the dynamic viscosity of the gas (Pa s), D_g is the diffusion coefficient of the absorbed component in the unabsorbed gas (m^2/h), w_g is the gas velocity (m/s), and $p_{1.g}$ is the mean partial pressure of the unabsorbed component in the gas (10^6 Pa).

For low concentrations of the absorbed component in the gas mixture we have $p_{l.g} \approx P$ and $\mathrm{Nu}'_g = k_g d_e P M_g/\rho_g D_g$ where P is the total pressure of the gas mixture (10^6 Pa) and M_g is the molecular mass of the gas mixture.

The gas density is $\rho_g \approx 28 \times 273/22.4\ (273 + 20) = 1.16$ kg/m^3, the gas viscosity is $\mu_g = 0.0175$ centipoise $= 0.0175 \times 10^3$ Pa s. Hence, we obtain $\mathrm{Re}'_g = 2220$, $\mathrm{Pr}'_g = 1.32$ ($D_g = (293/273)^{3/2} \times \times 0.122 \times 3600/10^4 = 0.049$ m^2/h (see Appendix II)).

Substitution of the Re'_g and Pr'_g values in Eq. (VII.70) yields $\mathrm{Nu}'_g = 14.1$.

Since $d_e = 4 \times 0.58/41.7 = 0.0556$ m we can write

$$k_g = \mathrm{Nu}'_g \rho_g D_g/d_e P M_g = 4.4 \text{ kmole/m}^2\text{h } 10^6 \text{ Pa}$$

Problem 17. Calculate the efficiency of one bed of the froth apparatus for absorption by solar oil of the benzene hydrocarbons from the coke-oven gas (absorption of high-solubility gases). The gas velocity is 1.5 m/s, the height of the froth layer is 0.15 m, the initial concentration of the benzene hydrocarbons in the gas is 36 g/m^3, the temperature in the absorption zone is 30 °C, the pressure in the apparatus is P $= 1.01 \times 10^5$ Pa.

Solution. For high-solubility gases the efficiency of absorption in the froth layer can be found from the equation for the equilibrium-approach criterion $\mathrm{Pa}_g = \ln \frac{1}{1-\eta_g}$ (see Eq. (VII.21)):

$$\mathrm{Pa}_g = 5.3 \left(\frac{w_g^3}{\nu_g g}\right)^{-0.04} \left(\frac{\nu_g}{D_g}\right)^{-0.2} \left(\frac{\psi}{P}\right)^{-0.2} \left(\frac{H_f}{d_e}\right)^{0.45} \qquad \text{(VII.71)}$$

Here $\eta_g = (Y_1 - Y_f)/(Y_1 - Y_m^*)$ is the efficiency of the mass transfer apparatus with respect to the gaseous phase; Y_1 and Y_f are the concentrations of the absorbed component in the gaseous phase at the beginning and the end of the process, respectively (g/m^3); Y_m^* is the concentration of the absorbed component in the gaseous phase which is at equilibrium with the mean concentration of the absorbed component in the liquid (g/m^3); w_g is the gas velocity (m/s); ν_g is the kinematic viscosity of the gas (m^2/s); g is the gravitational acceleration (m/s^2); D_g is the diffusion coefficient of the absorbed component in the gaseous phase (m^2/s); ψ is the Henry's law coefficient for the system (Pa); P is the overall pressure in the system (Pa); H_f is the height of the froth layer (m); d_e is the equivalent diameter of the apparatus (since the diameter does not affect froth formation it is typically assumed that the cross-section area of the apparatus is 1 m^2 so that $d_e = 1.13$ m).

Figure 30 presents a nomogram for solving Eq. (VII.71) from which it is easy to calculate the efficiency of a froth absorber.

First we have to calculate the following parameters using the constant values from the handbooks (see, for instance, [8]):

$$R_w = w_g^3 \rho_g / g^2 \mu_g = 1.5^3 \times 0.45/9.81^2 \times 1.33 \times 10^{-6} = 11\,800$$

$$Pr'_g = \mu_g g / \rho_g D_g = 1.33 \times 10^{-6} \times 9.81/0.45 \times 8.3 \times 10^{-6} = 3.5$$

$$M = \psi/P = 3.88 \times 10^4/10.1 \times 10^4 = 0.385$$

$$Pr'_g M = 1.35$$

To find the efficiency of the froth absorber from the nomogram of Fig. 30 pass a straight line through the point 1.35 on the axis Pr'_g

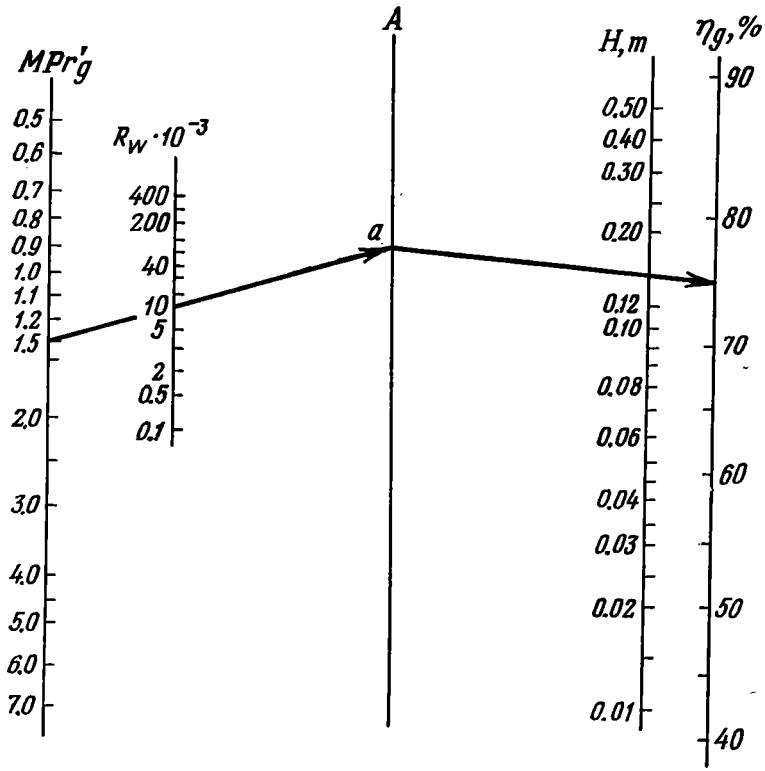


Fig. 30. Nomogram for determination of absorption efficiency of one bed of the foam apparatus.

and the point 11 800 on the axis R_w and find the intersection point a on the axis A. Then pass a straight line through the point a and the point 0.15 on the axis H_f and find the point of its intersection with the axis η_g which yields the efficiency value. In our case we have $\eta_g = 74.5\%$.

Problem 18. Find the efficiency of a bed of a froth apparatus for desorption of ammonia from a weak ammonia liquor by live steam. The consumption of steam per 1 kg of the liquid is 0.2 kg, the height of the froth layer is 0.15 m, and $P = 1.01 \times 10^5$ Pa.

Solution. The efficiency of desorption of high-solubility gases can be found from the equation for the equilibrium-approach criterion $\mathrm{Pa}_l = \ln \frac{1}{1-\eta_l}$ (see Eq. (21)):

$$\mathrm{Pa}_l = 4.84 \left(\frac{G}{L}\right)^{0.4} \left(\frac{\nu_g}{D_g}\right)^{-0.2} \left(\frac{\psi}{P}\right)^{-0.2} \left(\frac{H_f}{d_e}\right)^{0.45} \quad \text{(VII.72)}$$

Here $\eta_l = (X_f - X_i)/(X^* - X_i)$ is the efficiency of desorption with respect to the liquid phase, X_i and X_f are the initial and final

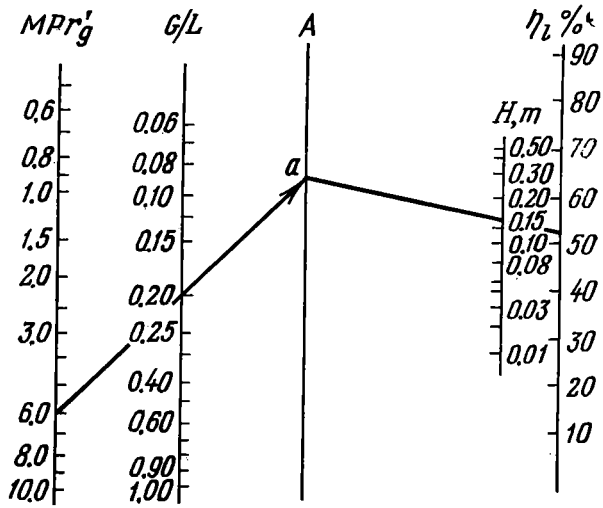


Fig. 31. Nomogram for determination of desorption efficiency of one bed of the foam apparatus.

concentrations of the desorbed component, respectively (g/m³); X^* is the equilibrium concentration of the desorbed component in the liquid under the given conditions (g/m³); G is the flow rate of steam (kg/h); L is the flow rate of the liquid (kg/h) and other parameters are given in Problem 17.

Figure 31 presents a nomogram based on Eq. (VII.72) which readily yields the efficiency values.

First, we find $\mathrm{Pr}'_g = 0.62$. For the weak ammonia solutions (NH_3 concentrations less than 2 g/kg) we can assume that the system satisfies Henry's law. We find from handbooks $\psi = 9.9 \times 10^5$ Pa. Then

we have $M = 9.9 \times 10^5/1.01 \times 10^5 = 9.8$ and $Pr'_g M = 6.1$. Plotting the straight lines through the respective points in Fig. 31 as it is done in Fig. 30 we can find the efficiency of the apparatus which is in our case $\eta_1 = 53\%$.

Problem 19 (see [22], p. 150). Calculate the area of the interface between the phases in the column for absorption of ammonia from a gas mixture by a sulphuric acid solution.

The starting partial pressure of ammonia in the gas mixture is 0.005×10^6 Pa and the final pressure is 0.001×10^6 Pa. The initial concentration of sulphuric acid in the column is 0.6 kmole/m^3 and the final concentration is 0.5 kmole/m^3. The mass transfer coefficient for gas is $k_g = 3.5$ kmole/m^2 h 10^6 Pa, the mass transfer coefficient for liquid is $k_l = 0.005$ m^2/h, and the Henry's law coefficient is $\psi = 750$ kmole/m^2 10^6 Pa. The flow rate of the gas mixture is 45 kmole/h and the overall pressure is 0.1×10^6 Pa. Absorption is carried out under counterflow conditions. The reaction has a high rate and is practically irreversible. It can be described by equation

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

Solution. For the reaction between a gaseous component A and a component B in the liquid phase described by the equation

$$aA + bB \rightarrow dD$$

the absorption rate is given by

$$u_{ab} = \frac{p_A + \frac{1}{m\psi}\frac{D_B}{D_A} C_B}{\frac{1}{k_g} + \frac{1}{\psi k_l}} \qquad \text{(VII.73)}$$

where u_{ab} is the amount of the component A transferred from the gas to the liquid per unit area of the phase interface per unit time, or the rate of absorption (kmole/m^{2}h), p_A is the partial pressure of the component A in the gas mixture (10^6 Pa), C_B is the concentration of the reactant B in the liquid (kmole/m^3), D_A and D_B are the diffusion coefficients of the components A and B (m^2/h), and $m = b/a$.

Eq. (VII.73) is valid if the concentration C_B is lower than the critical concentration C_B^{cr} of the reactant B in the liquid at which the phase interface and the reaction surface are identical.

When $C_B \geqslant C_B^{cr}$ we have

$$u_{ab} = k_l p_A \qquad \text{(VII.74)}$$

In this case the critical concentration of the reactant B in the absorbing liquid is

$$C_B^{cr} = m \frac{D_A}{D_B} \frac{k_l}{k_g} p_A \qquad \text{(VII.75)}$$

The numerator in Eq. (VII.73) describes the driving force of the process while the denominator is the overall resistance to the process expressed in the same terms as in the case of physical absorption.

Since $1/k_g + 1/\psi k_l = 1/K_M$ where K_M is the overall mass transfer coefficient we can write Eq. (VII.73) in the form

$$u_{ab} = K_M (p_A + qC_B) \qquad \text{(VII.76)}$$

where $q = (1/m\psi)(D_B/D_A)$.

For our process we find from Eq. (VII.75) $C_B^{cr} = 350p_A$ (we assume $D_A = D_B$).

At the bottom of the apparatus

$$C_B^{cr} = 350 \times 0.005 = 1.75 \text{ kmole/m}^3 (> 0.5)$$

and at the top of the apparatus

$$C_B^{cr} = 350 \times 0.001 = 0.35 \text{ kmole/m}^3 (< 0.6)$$

To simplify calculations we shall divide the apparatus into two regions—in the lower region $C_B < C_B^{cr}$ and in the upper region $C_B > C_B^{cr}$. The division line is at the level of the apparatus where C_B^{cr} equals the concentration of sulphuric acid.

The amounts of absorbed ammonia and reacted sulphuric acid can be found from the material balance: $45\,(0.005 - 0.001)/0.1 = 1.8$ kmole/h of NH_3 and $1.8/2 = 0.9$ kmole/h of H_2SO_4 or $0.9/(0.6 - 0.5) = 9$ m³/h of H_2SO_4.

The division line between the regions can be found from the balance equation for the lower region: $45\,(0.005 - p_A)/0.1 = 2 \times 9\,(C_B^{cr} - 0.5) = 2 \times 9\,(350p_A - 0.5)$ so that $p_A = 0.00166 \times 10^6$ Pa and $C_B^{cr} = 350 \times 0.00166 = 0.58$ kmole/m³.

Substituting $q = 1/0.5 \times 750 = 0.00267$ in Eq. (VII.76) we can find the driving force Δ_1' for the lower region and Δ_2' for the upper region: $\Delta_1' = 0.005 + 0.00267 \times 0.5 = 0.00633 \times 10^6$ Pa and $\Delta_2' = 0.00166 + 0.00267 \times 0.58 = 0.00321 \times 10^6$ Pa.

The mean driving force of the process is $\Delta_m' = (0.00633 + 0.00321)/2 = 0.00477 \times 10^6$ Pa.

The overall mass transfer coefficient K_M can be found from the equation $1/K_M = 1/k_g + 1/\psi k_l = 1/3.5 + 1/750 \times 0.005$. We find $K_M = 1.8$ kmole/m² h 10^6 Pa.

Hence, Eq. (VII.76) yields for the lower region $u_{ab}' = 0.0083$ kmole/m² h. For the upper region it is usual to calculate the driving force at the top and at the bottom of the region: $\Delta_1'' = 0.00166 \times 10^6$ Pa and $\Delta_2'' = 0.001 \times 10^6$ Pa so that $\Delta_m'' = (0.00166 + 0.001)/2 = 0.00133 \times 10^6$ Pa.

Hence, the rate of the process in the upper region is $u''_{ab} = 0.00465$ kmole/m² h.

The amount of ammonia absorbed in the lower region is 45 (0.005 — — 0.00166)/0.1 = 1.5 kmole/h and that for the upper region is 1.8 — 1.5 = 0.3 kmole/h.

The contact surface area of the lower region is $F' = 1.5/0.0083 = 180$ m² and that of the upper region is $F'' = 0.3/0.00465 = 65$ m². The total contact surface area of the apparatus should be $F = 245$ m².

Problem 20. Calculate the parameters of the froth apparatus for scrubbing the gas produced with electrolysis of $MgCl_2$. The process should provide for cooling of the gas to reduce the moisture content in it.

The flow rate of the gas containing 70% chlorine is 800 m³/h. The starting temperature of the gas is 40 °C, the temperature of water is 10 °C. The dust content is 5.6 g/m³ (chlorides of Mg, Ca, Na, and K). The dust particles are assumed to have the sizes of 10-20 μm. The residual dust content in the gas is 0.04 g/m³. The moisture content of the gas is 4.0 g/m³.

Solution. Assume that the overall pressure of the gas is 0.975 × × 10^5 Pa. Then the gas volume under the process conditions is 800 (273 + 40) × 100 000/273 × 97 500 = 930 m³/h. The respective amount of moisture is 4.0 × 930 = 3720 g/h. The amount of dust in the gas is 5.6 × 930 = 5200 g/h. The volume of the water vapour in the gas is 3720 × 22.4/18 × 1000 = 5 m³/h. The volume of the dry gas is 800 — 5 = 795 m³/h.

Since the typical temperature difference between gas and liquid discharged from a froth apparatus is 3-5 K we can assume that the temperature of the discharged gas is 13 °C (taking into account the requirement for cooling the gas).

Assuming that the pressure difference in the apparatus is approximately 1600 Pa (12 mm Hg) we can find the volume of the dry gas discharged from the apparatus:

$$795 (273 + 13) \times 100\,000/273 (100\,000 - 1600) = 855 \text{ m}^3/\text{h}$$

The partial pressure of the water vapour at 13 °C is 1490 Pa (11.2 mm Hg) (see, for instance, [7, 8]). The water content in the discharged gas is 1490 × 100/(100 000 — 1600) = 1.5%.

The volume of the gas discharged from the apparatus is 855 × × 100/(100 — 1.5) = 868 m³/h. The volume of the water vapour in the gas discharged from the apparatus is 868 — 855 = 13 m³/h. The moisture content of the discharged gas is 13 × 273 (100 000 — — 1600) 18 × 1000/(273 + 13) 100 000 × 22.4 × 868 = 11 g per 1 m³ of wet gas.

The amount of water discharged with the gas is 11 × 868 = = 9550 g/h.

The amount of dust in the discharged gas is 0.04 × 868 = 35 g/h.

To provide for the specified degree of scrubbing the efficiency of the apparatus should be

$$\eta = ((5200 - 35)/5200) \times 100 = 99.3\%$$

Calculations of the Process Conditions and the Parameters of the Apparatus

The performance of a froth scrubber is, to a large extent, determined by the gas velocity w_g in it. The optimum range of the gas velocity and its effects on scrubbing of dust of various types under experimental and industrial conditions have been discussed in the monograph [27].

We shall assume $w_g = 2.0$ m/s (under the grate) taking into account some decrease in the discharged gas volume, prevention of droplet ejection (which can occur at high gas velocities), the need for decreasing the hydraulic resistance of the scrubber and a possibility of a $\pm$ 25% variation of the apparatus capacity. First we shall calculate the height of a single froth bed providing for the required efficiency of scrubbing.

The coefficient of scrubbing rate K (in m/s) is given by the following formula:

$$K = \frac{2\eta w_g}{2 - \eta}$$

Since $\eta = 0.993$ we find $K = 3.94$ m/s. The height H_f of the froth layer (for capture of hydrophilic dust with the particle size of 15-20 μm) is related to K by the following empirical formula:

$$K = H_f + 1.95 w_g - 0.09 \qquad \text{(VII.77)}$$

Hence, we obtain $H_f = 0.13$ m. For the dust scrubbers H_f can be estimated from the following formula:

$$H_f = 0.65 w_g (h_0 + 0.015) + 2h_0$$

Here h_0 is the height of the starting layer of the liquid. For our scrubber we obtain $h_0 = 0.035$ m.

The cross-section area of the scrubber is $S = 930/3600 \times 2.0 = 0.13$ m^2. The cross section of the apparatus can be circular or rectangular according to technological requirements. For the circular cross section we have the diameter of 0.41 m. For a small-capacity scrubber the rectangular cross section is more convenient. Then the size of the apparatus is $a = b = 0.36$ m. If the cross section of the scrubber is constant the velocity of the gas discharged from the apparatus is $w_g = 868/3600 \times 0.13 = 1.85$ m/s which is reasonable.

Experimental results and industrial experience show that the consumption of water for scrubbing the gas with a medium dust content (not more than 10 g/m³) and at a temperature below 100 °C varies between 0.2 and 0.3 litre/m³. Since gas must be cooled in our process we shall assume that the consumption of water is 1 litre/m³.

Then the flow rate of water is $L = 1 \times 930/1000 \approx 1$ m³/h. The intensity i of the water flow is $1/0.36 = 2.8$ m³/m h if the water flows throughout the width of the grate (typically, i varies between 1 and 5 m³/m h). The height of the water layer h_0 depends on the lip height h_l and the height h_w of the water layer over the lip:

$$h_0 = \psi_h h_l + 3\varepsilon \sqrt[3]{i^2} \qquad \text{(VII.78)}$$

where ψ_h is the froth head coefficient which varies between 0.4 and 1 and here is taken to be 0.6, ε is the factor of increase in the size of the water layer owing to the effect of the grate producing additional resistance to its motion (here $\varepsilon = 1$; see Appendix XII).

Then we obtain

$$h_l = (35 - 3\sqrt[3]{2.8^2})/0.6 = 50 \text{ mm}$$

We shall make use of the grate of the type 12/6 (here the numerator is the spacing t (mm) between the centres of the holes and the denominator is the hole diameter d_0 (mm)). The area of the holes of the grate amounts to

$$S_0 = 91 d_0^2/t^2 = 91 \times 6^2/12^2 = 22.7\%$$

The gas velocity w_0 at the holes of the grate is

$$w_0 = w_g \times 100/S_0 z$$

where z is the relative area of the perforated part of the grate ($z = 0.9$). Hence we obtain $w_0 = 10$ m/s which is reasonable for dust removal.

The following formula has been found for the hydrophilic dust:

$$\eta = 0.89 \left[\frac{w_g i}{3600 g (0.1 - h_l)^2}\right]^{0.005} \left(\frac{\rho \delta^2 w_g}{g \mu d_0}\right)^{0.04} \qquad \text{(VII.79)}$$

Here ρ is the apparent density of the dust (kg/m³), δ is the mean size of the dust particles (m), and μ is the gas viscosity (Pa s).

Since the parameters of the dust are not known precisely we can make use of a modification of Eq. (VII.79):

$$\eta = 1.01 \left[\frac{w_g i}{3600 g (0.1 - h_l)^2}\right]^{0.005} \qquad \text{(VII.80)}$$

Equation (VII.80) is applicable to the removal of hydrophilic dust particles with the mean size of 15 μm. Equation (VII.80) yields $\eta = 0.995$ which is in a good agreement with the specified efficiency of the scrubber.

The total hydraulic resistance of the scrubber is

$$\Delta P = \Delta P_{d.g} + \Delta P_f + \Delta P_{ap} \qquad \text{(VII.81)}$$

where $\Delta P_{d.g}$ is the resistance of the dry grate, ΔP_f is the resistance of the froth layer, and ΔP_{ap} is the resistance at the inlet and outlet of the apparatus plus the resistance of the spray trap which are taken to be 100 Pa each. The resistance of the dry grate is

$$\Delta P_{d.g} = 1.45 \frac{\rho_g}{2} w_0^2 \qquad \text{(VII.82)}$$

where ρ_g is the density of the gas. Hence, $\Delta P_{d.g} = 1.45\ (0.7 \times \times 3.233 + 0.3 \times 1.243)\ 273 \times 97\ 500 \times 10^2/2\ (273 + 40) \times 10^5 = = 170$ Pa. The resistance of the froth layer is

$$\Delta P_f = (325 H_f - 23 w_g + 43.5)\, g = 400 \text{ Pa}$$

Hence, the total hydraulic resistance of the scrubber is $\Delta P = 870$ Pa (8 mm Hg) which does not differ very much from the value assumed in the above calculations.

Problem 21. Calculate a froth apparatus for drying chlorine gas with 93% sulphuric acid. The final moisture content in the gas should be not more than 0.04% (by mass). The apparatus should produce 750 m^3/h of dry gas. The initial gas temperature is 13 °C, the flow rate of wet gas is 819 m^3/h, the moisture content is 11 g per 1 m^3 of wet gas, or 9.0 kg of H_2O per hour.

Solution. *Material balance.* Assume that the gas volume in the apparatus does not change (the effects of pressure and temperature are ignored). The mass flow rate of gas is $750 \times 3.233 = 2420$ kg/h. As the moisture content of the dry gas is 0.04% (by mass) the discharged gas contains $2420 \times 0.04/(100 - 0.04) = 0.97$ kg/h or $0.97 \times 22.4/18 = 1.2$ m^3/h.

Assume that the final concentration of sulphuric acid after one-cycle absorption of moisture from gas is 78%.

The water content in the starting acid is $(1 - 0.93)/0.03 = = 0.075$ kg per 1 kg of 100% acid and that in the final acid $(1 - 0.78)/0.78 = 0.282$ kg per 1 kg of 100% acid. Hence, 1 kg of 100% acid absorbs $0.282 - 0.075 = 0.207$ kg of water. The consumption of 100% acid is $(9 - 0.97)/0.207 = 38.8$ kg/h. Hence, the consumption of 93% acid is $38.8/0.93 = 41.7$ kg/h and the amount of discharged acid is $38.84/0.78 = 49.7$ kg/h. The consumption of 93% sulphuric acid for drying 1 ton of chlorine is $41.7/2.420 = 17.3$ kg.

Heat balance. Absorption of water by sulphuric acid results in liberation of heat. The heat of dissolution of 1 kg of 93% sulphuric acid to 78% concentration is 213.3 kJ (calculated by the Thomson rule). The total heat liberated with dissolution is $213.3 \times 41.7 = = 8882$ kJ/h. For simplicity assume that the heat is consumed only for heating of the acid and chlorine (that is, ignore the heat losses in

the apparatus). Then the increase in the temperature of acid and chlorine during drying is 8882/4.19 (2420 × 0.124 + 49.7 × 0.358) = = 6.7 K. This temperature increase is technologically admissible, the more so as the heat losses have not been taken into account.

Apparatus parameters. The efficiency of the apparatus can be determined from the specified gas parameters:

$$\eta = (9 - 0.97)/9 = 0.9$$

(we ignore the partial pressure of the water vapour over the starting sulphuric acid). According to the experimental results the efficiency of one bed in a froth drying apparatus can be taken to be 80%. Then the required number of beds in the apparatus is

$$n = \log (1 - 0.9)/\log (1 - 0.8) \approx 2$$

Taking into account possible deterioration of the apparatus parameters under industrial plant conditions and the differences in bed efficiencies we shall assume that the apparatus has 3 beds.

The gas velocity in the apparatus w_g is taken to be 1.75 m/s; this value takes into account the experimental results, a possible ±25% variation of the gas flow rate, and the requirements of the optimum hydraulic resistance and the lack of spraying.

At each bed the froth layer should have the height $H_f = 0.2$ m to provide for the specified efficiency of the apparatus. Under the process conditions the height of the froth layer is given by the following equation:

$$H_f = 0.7 w_g (h_0 - 0.012) + 1.75 h_0 \qquad \text{(VII.83)}$$

Here h_0 is the height of the starting liquid layer. From Eq. (VII.83) we find the height of the starting acid layer for the froth height of 0.2 m on all the beds: $h_0 = 0.06$ m.

The flow rate of the wet gas is 819 m³/h. Since the gas velocity is 1.75 m/s we can find the cross-section area of the apparatus $S =$ $= 819/3600 \times 1.75 = 0.13$ m². For the circular cross section the diameter is 0.4 m. However, a rectangular cross section provides for a better distribution of liquid over the grate. We shall assume a 270 × 480 mm rectangular cross section.

The intensity of the acid flow at the lower grate is $i =$ $= 49.7/1704 \times 0.27 = 0.11$ m³/m h (here 1704 kg/m³ is the density of the 78% sulphuric acid and 0.27 m is the length of the drain. We shall assume $i = 0.10$ m³/m h throughout the process.

The lip height is given by

$$h_l = (h_0 + 3\varepsilon \sqrt[3]{i^2})/\psi_h \qquad \text{(VII.84)}$$

Here we have $h_0 = 60$ mm and we can assume $\varepsilon = 1$ and $\psi_h = 0.5$ (see Appendix IV). Then we obtain $h_l = 120$ mm.

The convenient type of grate to be used in the apparatus is 6/3 for all the beds (see Problem 20). The relative free cross-section area of the 6/3 grate amounts to 22.7%. The gas velocity in the grate holes is $w_0 = 1.75 \times 100/22.7 = 7.7$ m/s. We assume here that the area of the perforated part of the grate equals the free cross-section area of the apparatus. We consider this gas velocity acceptable taking into account the small diameter of the grate holes, the high gas density, and the high viscosity of sulphuric acid.

The partial pressure of water vapour in the gas is 1490 Pa at the inlet and 160 Pa at the outlet and the pressure of water vapour over the acid is 200 Pa at the inlet and 2.7 Pa at the outlet. Hence, the driving force of absorption of water vapour by sulphuric acid is

$$\Delta P_m = \frac{(1490-200)-(160-2.7)}{2.3 \log \frac{1490-200}{160-2.7}} = 545 \text{ Pa}$$

The amount of water absorbed by the acid is $9 - 0.97 = 8.03$ kg/h.

Under the conditions of the process the coefficient of absorption of water vapour by sulphuric acid is on the average 0.0565 kg/m² h Pa (calculated for the area of the grate). Hence the total area of the grates should be $8.03/545 \times 0.0565 = 0.26$ m².

In our apparatus the total area of the grates is $3 \times 0.13 = 0.39$ m², that is, more than enough for the specified efficiency.

Problem 22. A. Calculate the absorption coefficient for absorption of hydrogen fluoride by 3-5% Na_2CO_3 solution in the apparatus with two fluidized packing beds. The gas flow rate is 100 000 m³/h, the initial concentration of hydrogen fluoride in the gas is 0.1 g/m³, the final concentration is 0.002 g/m³. The gas temperature is 70 °C at the inlet and 20 °C at the outlet. The apparatus diameter is 2.5 m. The height H'_{st} of the static bed of packing on each grate is 0.3 m.

B. Calculate the height of the packing bed H'_{st} needed for absorption efficiency $\eta = 0.985$ in the apparatus with two fluidized packing beds and the hydraulic resistance of the absorption zone. The gas velocity is $w_g = 5.5$ m/s, the irrigation density is $L = 10$ m³/m² h, and the density of the packing particles is $\delta = 200$ kg/m³.

Solution. A. The apparatus with irrigated fluidized packing bed is a cylindrical column with one or several perforated, slit or grid grates supporting beds of hollow-sphere packing.

The gas is fed under the lower grate and liquid flows from the top so that over each grate a turbulized gas-liquid bed is formed with the packing particles increasing the area of the interphase interface. According to the gas velocity there are three main hydrodynamic regimes in the apparatus—static packing bed, beginning of suspension of the packing, and fluidized-bed regime. The fluidized-bed regime provides for the optimum conditions for the mass-exchange processes.

The gas velocity in the apparatus under the specified conditions is $w_g = 100\,000/3600 \times 0.785 \times 2.5^2 = 5.5$ m/s. The efficiency of the absorption process is given by Eq. (VII.17):

$$\eta = (C_1 - C_t)/C_1 = (0.1 - 0.002)/0.1 = 0.98$$

The rate constant for absorption of hydrogen fluoride can be found from the equation of material balance

$$G_{ab} = V_g (C_1 - C_t)$$

where V_g is the gas flow rate (m^3/h) and G_{ab} is the amount of hydrogen fluoride absorbed per hour; and from Eq. (VII.23) for mass transfer

$$G_{ab} = k_{st} v_{st} \Delta C$$

where k_{st} is the rate constant of absorption for the static packing bed (1/h), v_{st} is the volume of the static packing layer (m^3), and ΔC is the driving force of absorption (g/m^3).

Since the partial pressure of HF over the Na_2CO_3 solution is zero the driving force is given by

$$\Delta C = (C_1 - C_t)/2.3 \log (C_1/C_t)$$

The efficiency of absorption depends on the absorption rate constant according to the following equation:

$$\eta = 1 - \exp (k_{st} H_{st}/3600 w_g) \qquad \text{(VII.85)}$$

The absorption rate constant is determined by the hydrodynamic conditions and can be written as

$$k_{st} = 4600 w_g^{1.2} L^{0.4} H_{st}^{-0.54} \qquad \text{(VII.86)}$$

If the apparatus has two beds of packing with $H'_{st} = 0.3$ m we obtain

$$H_{st} = 2H'_{st} = 0.6 \text{ m}$$

Equation (VII.85) yields $k_{st} \approx 129\,000$ 1/h.

B. Equations (VII.85) and (VII.86) yield

$$\eta = 1 - \exp (1 - 1.28 w_g^{0.2} L^{0.4} H_{st}^{0.46})$$

Hence, we obtain $H_{st} = 0.8$ m and $H'_{st} = 0.4$ m.

The hydraulic resistance ΔP of the absorption zone is given by $\Delta P = 2 \times 9.81 \Delta P_{st} = 2 \times 9.81 (0.3 \times 5.5^2 + 0.524 \times 200 \times 0.4) \times \times (1 + 0.68 \times 10^{-2} \times 10 \times 5.5 \times 1.2) = 1450$ Pa.

Problem 23. Determine the efficiency of the cross-current plate with annular valves (see Fig. 32) for the column with a diameter of 260 mm and the mass-transfer coefficient for desorption of carbon dioxide from its aqueous solution blown with the air. The CO_2 concentration is 0.65 g/litre in the solution fed to the plate and

0.12 g/litre in the solution discharged from the plate. The temperature at the plate is 20 °C. The irrigation density is $L = 15.1$ m³/m² h. The gas flow raises the valves so that the gap between the valve and the plate surface is $a_i = 6.5$ mm. The valve mass is $G_v = 0.03$ kg.

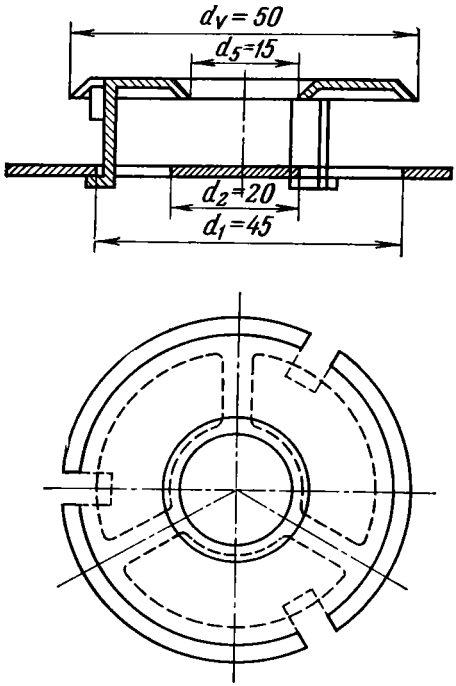


Fig. 32. The diagram of the annular valve (Problem 23).

The relative free surface area of the plate is $S_0 = 0.12$ m²/m². The height of the gas-liquid layer on the plate is $H = 130$ mm.

Solution. The gas velocity w_0 (in m/s) in the plate apertures under the valves can be found from the following formula*:

$$w_0 = \frac{8a_i}{1.55d_1^2(1-d_2/d_1)}\sqrt{\frac{G_v}{\pi\rho_g B}} \qquad \text{(VII.87)}$$

Here

$$B = \frac{d_2^2}{2d_1^2} + \frac{d_2^2}{d_1^2}\ln\frac{d_2}{d_3} + 0.5\frac{d_1^2}{d_2^2}\left(1-\frac{d_1^2}{d_v^2}\right) + \ln\frac{d_1}{d_v} - \frac{d_2^4 d_v^2}{2d_1^4 d_3^2} \qquad \text{(VII.88)}$$

For the conditions of our process Eq. (VII.88) yields $w_0 = 8$ m/s. The gas velocity in the column is

$$w_g = w_0 S_0 = 0.916 \text{ m/s}$$

* Tarat, E. Ya., *et al.*, *Zhurn. prikl. khimii*, vol. XLV, No. 9, 1989-1993 (1972).

The Reynolds criterion for the gas and liquid can be written as

$$\mathrm{Re_g} = \frac{w_g \rho_g l}{\mu_g} \quad \text{and} \quad \mathrm{Re_l} = \frac{L \rho_l l}{3600 \mu_l}$$

where l is the geometric parameter of the valve:

$$l = \left(\frac{a}{d_1 - d_2}\right) d_1 = \frac{8}{45 - 20} 0.045 = 0.014 \text{ m} \qquad \text{(VII.89)}$$

We obtain $\mathrm{Re_g} = 850$ and $\mathrm{Re_l} = 45$.

The equilibrium-approach criterion is given by the following formula*:

$$\mathrm{Pa_l} = 0.8 \mathrm{Re_g^{0.36}} \mathrm{Re_l^{-0.52}} (H/a_1)^{0.23} S_0^{0.18} k^{0.36} \qquad \text{(VII.90)}$$

where k is a dimensionless parameter of the valve:

$$k = a/(d_1 - d_2) = 0.32 \qquad \text{(VII.91)}$$

Then we obtain $\mathrm{Pa_l} = 1.13$.

The equilibrium-approach criterion can also be determined with a sufficient accuracy from the nomogram of Fig. 33. The equation

$$\mathrm{Pa_l} = \ln (1/(1 - \eta_l))$$

yields $\eta_l = 0.81$.

The mass-transfer coefficient for the plate can be found from the following equation:

$$\mathrm{Pa_l} = \ln \frac{1}{1 - \eta_l} = 0.735 \frac{K_M}{L} \qquad \text{(VII.92)}$$

We obtain $K_M = 23.3$ m/h.

Problem 24. Calculate the rate of chlorination of aluminium oxide in molten chlorides in the presence of petroleum coke if the consumption of pure chlorine is 100 litres/h and the gas products of chlorination after condensation of aluminium chloride vapour contain 80% (by volume) of chlorine and 20% (by volume) of carbon dioxide. The process is carried out under the pressure of 10^5 Pa (760 mm Hg).

Solution. Chlorination of aluminium oxide in molten chlorides is described by the following reaction:

$$2Al_2O_3(\text{solid}) + 3C(\text{solid}) + 6Cl_2(\text{gas}) = 4AlCl_3(\text{gas}) + 3CO_2(\text{gas}) \qquad \text{(VII.93)}$$

The gas products of chlorination after removal of aluminium chloride consist of carbon dioxide and unreacted chlorine. The reaction equation shows that 6 moles of reacted chlorine give rise to 3 moles of carbon dioxide. Hence, the reaction decreases the volume of the gaseous phase by a factor of 2. Therefore, the starting volume of chlorine is

$$v'_{Cl_2} = 2v_{CO_2} + v_{Cl_2} \qquad \text{(VII.94)}$$

* Segal, V. A., Thesis, Leningrad Technology Institute, 1973.

where v_{CO_2} and v_{Cl_2} are the volumes of carbon dioxide and chlorine in the gaseous products of the reaction.

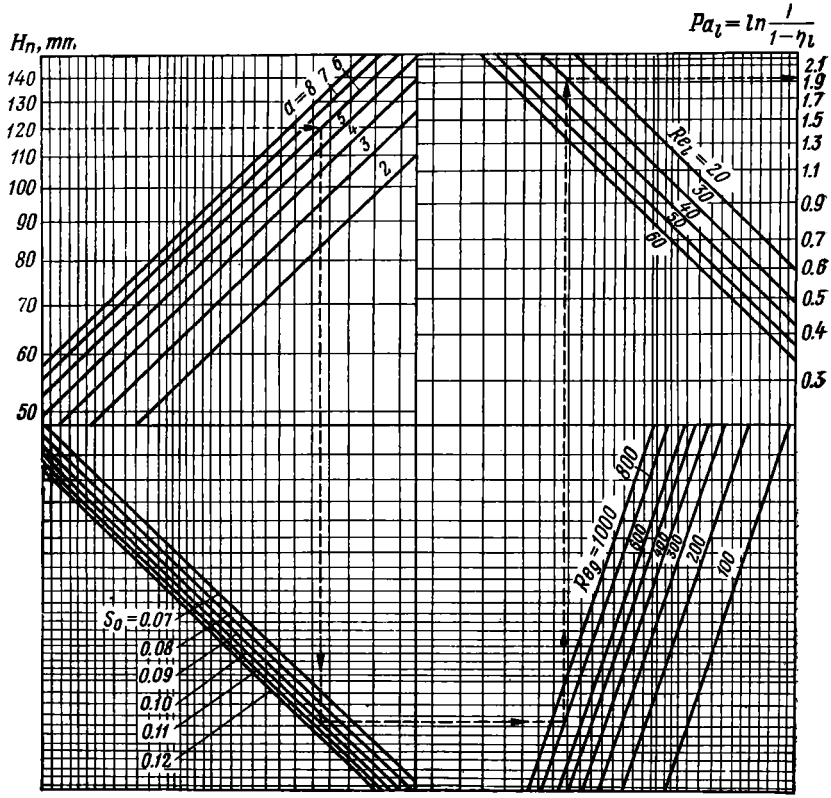


Fig. 33. Nomogram for determination of the efficiency of the plates with annular valves for desorption of sparingly soluble gases.

The ratio between the volumes of carbon dioxide and chlorine is equal to the ratio between their concentrations, % (by volume):

$$\frac{v_{Cl_2}}{v_{CO_2}} = \frac{[Cl_2]}{[CO_2]} \qquad \text{(VII.95)}$$

The volume of chlorine in the gaseous reaction products can be found from Eqs. (VII.94) and (VII.95) and then from the equation

$$\eta = \frac{v'_{Cl_2} - v_{Cl_2}}{v'_{Cl_2}} \times 100 \qquad \text{(VII.96)}$$

we find the coefficient of utilization of chlorine $\eta = 33.4\%$. The rate of chlorination of aluminium oxide (in g/h) is given by the follow-

ing equation:

$$u = 1.52 \times 10^{-2} v'_{Cl_2} \eta \qquad \text{(VII.97)}$$

Here 1.52×10^{-2} is the factor for conversion from the volume of reacted chlorine to aluminium oxide according to Eq. (VII.93).

We obtain $u = 1.52 \times 10^{-2} \times 100 \times 33.4 = 51$ g/h.

Problem 25. When aluminium oxide is chlorinated in the molten chlorides in the presence of coke the melt absorbs chlorine which reacts with aluminium oxide and carbon.

Calculate the mass-transfer coefficient in absorption of chlorine if the cross-section area of the reactor is $S = 33.2 \times 10^{-4}$ m^2, the mean bubble diameter is $d = 0.005$ m, the gas saturation coefficient for the melt is $\varphi = 0.113$, and the coefficient of utilization of chlorine is 34%. The consumption of 100% chlorine is 100 litres/h. The height of the melt layer in the reactor is $h = 0.62$ m.

Solution. Equation (VII.93) for the chlorination reaction shows that 6 moles of chlorine give rise to 7 moles of aluminium chloride and carbon dioxide. Therefore, we can assume that chlorination practically does not change the volume of the gaseous phase.

The volume of the gas bubbles in the melt is

$$v = h\varphi S = 2.3 \times 10^{-4} \text{ m}^3 \qquad \text{(VII.98)}$$

The surface area of the bubbles in the melt can be found from the volume v_b of a bubble:

$$F = \frac{v}{v_b} S_b = \frac{6v}{d} = 0.278 \text{ m}^2 \qquad \text{(VII.99)}$$

The amount of absorbed chlorine is

$$G_{Cl_2} = \frac{3.17 V \eta}{1000 \times 71 \times 100} = 0.446 \times 10^{-6} V \eta =$$
$$= 1.52 \times 10^{-3} \text{ kmole/h} = 4.22 \times 10^{-7} \text{ kmole/s}$$

where V is the flow rate of chlorine.

The mean logarithmic driving force of absorption is

$$\Delta p_m = \frac{(p_i - p_e) - (p_f - p_e)}{2.3 \log \frac{(p_i - p_e)}{(p_f - p_e)}} \qquad \text{(VII.100)}$$

where p_i, p_f, and p_e are the initial, final, and equilibrium partial pressures of chlorine, respectively (Pa).

If the density of the melt is 1500 kg/m^3 and its height is 0.62 m we have $p_i = 0.1 \times 1.096 = 0.1096 \times 10^6$ Pa, $p_e = 0$, and $p_f = 0.1 (1.0 - 1.0 \times 0.34) = 0.066 \times 10^6$ Pa.

Then Eq. (VII.100) yields $\Delta p_m = 0.0858 \times 10^6$ Pa.

The mass-transfer coefficient for chlorine absorption is given by the following equation:

$$k_g = \frac{G_{Cl_2}}{F\Delta p_m} = 6.36 \times 10^{-2} \text{ kmole/m}^2 \text{ h } 10^6 \text{ Pa} = 1.77 \times$$
$$\times 10^{-2} \text{ mole/m}^2 \text{ s } 10^6 \text{ Pa}$$

Problem 26. Calculate the reaction size of the apparatus for chlorination of titanium slag in molten chlorides. The consumption of chlorine is 170 tons a day. The starting gas contains 70% (by volume) of chlorine. The starting pressure of the gas is 0.15×10^6 Pa. The temperature of the melt is 800 °C. The partial pressure of chlorine in the discharged gas is 0.0002×10^6 Pa, the pressure of the discharged gas-vapour mixture is 0.1×10^6 Pa, and the equilibrium partial pressure of chlorine in the gas over the melt is 0.00015×10^6 Pa. The mean diameter of the gas bubble in the melt is 5 mm. The mass-transfer coefficient for chlorine absorption by molten NaCl, $MgCl_2$, and iron chlorides has been found* to be $k_g = 1.0$ kmole/m² h 10^6 Pa.

Solution. Chlorination of titanium dioxide which comprises 85% of the titanium slag is described by the following equation:

$$TiO_2(\text{solid}) + 2Cl_2(\text{gas}) + C(\text{solid}) = TiCl_4(\text{gas}) + CO_2(\text{gas}) \quad \text{(VII.101)}$$

The reaction equation shows that 2 moles of chlorine give rise to 2 moles of gaseous reaction products so that the reaction does not change the volume of the gaseous phase.

The time of absorption (in seconds) of a chlorine bubble in the melt is

$$\tau = \frac{2.3 (\log p_i - \log p_f) v_b}{k_g F_b v_0} \quad \text{(VII.102)}$$

where p_i and p_f are the initial and final partial pressures of chlorine in the gas (10^6 Pa), k_g is the mass-transfer coefficient for absorption of chlorine by the melt (kmole/m² h 10^6 Pa), F_b is the surface area of the bubble (m²), and v_0 is the volume of 1 mole of chlorine at the temperature of the melt and the pressure 10^5 Pa.

Equation (VII.102) yields $\tau = 2.12$ s.

The plot in Fig. 34 can be used to find the vertical velocity of the gas bubble in the melt (w_v) with respect to the reactor wall from the velocity w of the gas fed to the reactor. We obtain $w_v = 1.67$ m/s if $w = 0.6$ m/s.

The height of the melt in the reactor is

$$H = \tau w_v = 3.4 \text{ m}$$

* A. B. Bezukladnikov, D. P. Baibakov, E. Ya. Tarat, *Tsvetnaya Metallurgiya*, No. 9, 30 (1974).

To rule out a possibility of incomplete absorption of the gas in the bubble we shall increase the height of the melt layer by the reserve factor of 1.5 so that $H = 5.1$ m.

To find the cross-section area S of the reactor we shall first calculate the gas flow rate per 1 m^2 of the reactor cross section:

$$G_{sp} = w\tau \frac{273}{273+t} \frac{M}{22.4} \qquad \text{(VII.103)}$$

where t is the temperature of the melt (°C), M is the molecular mass of chlorine (71), and $\tau = 24$ hours. We obtain $G_{sp} = 42$ tons of Cl_2

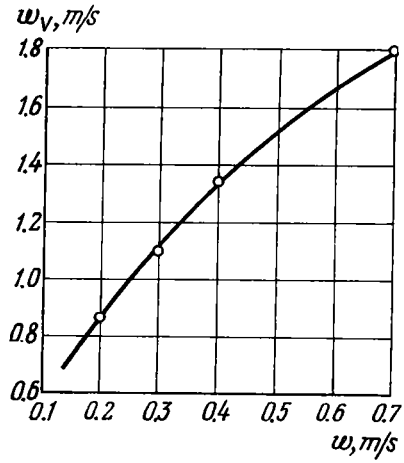


Fig. 34. The vertical velocity w_b of the floating-up gas bubbles as a function of the velocity of chlorine w in the free cross section of the chlorinator.

per 1 m^2 per 24 hours. Then the cross-section area of the reactor is $S = G/G_{sp} = 170/42 = 4$ m^2 (here G is the total flow rate of chlorine).

As shown by industrial experience the optimum distribution of chlorine in the melt can be obtained if the width of the chlorinator is 0.9 m. Then the length of the chlorinator is 4.4 m.

Calculations of the Mass Exchange Processes in the L-L, G-S, and L-S Systems

Problem 27. Calculate the amounts of picric acid dissolved in water and in benzene for a mixture of 300 ml of water, 200 ml of benzene, and 0.2 mole of picric acid. The coefficient of distribution of picric acid between water and benzene is 0.005.

Solution. According to the distribution law for a mixture of two mutually insoluble liquids the ratio between the concentrations of a component in each of the liquids is constant:

$$C_A/C_B = K \qquad \text{(VII.104)}$$

Here C_A is the concentration of the component in the liquid A (mole/litre), C_B is the concentration of the component in the liquid B (mole/litre), and K is the distribution coefficient.

If one of the liquids is water (for instance, A) and the dissolved component C is an electrolyte and is ionized in water we can transform Eq. (VII.104) into

$$C_A^m/C_B = K'$$

where m takes into account electrolytic dissociation of the dissolved component.

If the concentrations of picric acid are n_1 mole/litre in water and n_2 mole/litre in benzene the total amount of picric acid is $0.3n_1 + 0.2n_2 = 0.2$

Picric acid is an electrolyte for which $m = 2$ so that Eq. (VII.104) can be written as

$$n_1^2/n_2 = 0.005$$

Hence, we obtain

$$0.3n_1 + 0.2n_1^2/0.005 = 0.2$$

and $n_1 = 0.067$ mole/litre. Thus, 0.3 litre of water contains $0.067 \times 0.3 \approx 0.02$ mole of picric acid while 0.2 litre of benzene contains $0.2 - 0.02 = 0.18$ mole of picric acid, that is $0.18 \times 100/0.2 = 90\%$ of the total amount of the acid.

Problem 28 (see [2]). Carbon disulphide is used to extract iodine from the saturated aqueous solution. The coefficient of distribution of iodine between water and carbon disulphide is 0.0017. Calculate the concentration of iodine in 2 litres of the aqueous solution after stirring with 100 ml of carbon disulphide. Find how many 150-ml portions of carbon disulphide are needed to reduce the iodine concentration in water to 10^{-6} g/litre. Extraction is carried out at 20 °C when the iodine solubility in water is 0.03 g per 100 ml of water.

Solution. Iodine concentration in the saturated solution before extraction is 0.3 g/litre. For each litre of the solution 50 ml (0.05 litre) of carbon disulphide are taken. If the final concentration of iodine in the solution after extraction is C (g/litre) then the amount of iodine extracted by carbon disulphide is $0.3 - C$ (g/litre) and the iodine concentration in it is $(0.3 - C)/0.05$ (g/litre).

Then the distribution coefficient is

$$K = C_1/C_2 = C/((0.3 - C)/0.05) = 0.0017$$

Hence we obtain $C = 0.01$ g/litre, that is, extraction of iodine from 2 litres of the saturated aqueous solution with 100 ml of carbon disulphide reduce the iodine concentration in water to 0.01 g/litre.

Similar calculations yield the following formula for the iodine concentration C_n in the aqueous solution after the nth extraction cycle:

$$C_n = \left(\frac{0.00051}{0.05+0.0017}\right)^n \qquad \text{(VII.105)}$$

Equation (VII.105) has the following general form:

$$C_n = C_1 \left(\frac{K}{K+v}\right) \qquad \text{(VII.106)}$$

Here C_1 is the initial concentration of the dissolved component in the starting solution (g/litre) and v is the volume of the extractant per 1 litre of the first solution.

Equation (VII.105) for $C_n = 10^{-6}$ g/litre yields $n \approx 3$.

Problem 29. Using the data on the composition of the equilibrium mixtures (Table 39) plot the following phase diagrams for the system

TABLE 39

Composition of the Equilibrium Mixture
(R—water layer, E—chlorobenzene layer)

Point on triangular diagram	x_A	x_B	x_C	Point on triangular diagram	y_A	y_B	y_C
1	99.89	0	0.11	*1′*	0.18	0	99.82
2	89.79	10	0.21	*2′*	0.49	10.79	88.72
3	79.69	20	0.31	*3′*	0.79	22.23	76.98
4	69.42	30	0.58	*4′*	1.72	37.48	60.80
5	58.64	40	1.36	*5′*	3.05	49.44	47.51
6	46.28	50	3.72	*6′*	7.24	59.19	33.57
7	27.41	60	12.59	*7′*	22.85	61.07	15.08
8	25.66	60.58	13.76	*8′*	25.66	60.58	13.76

water (A)-acetone (B)-chlorobenzene (C): (a) triangular diagram; (b) in the X-Y coordinates; and (c) in the X-Z, Y-Z' coordinates. Here

$$X = \frac{x_B}{x_A+x_B}, \quad Y = \frac{y_B}{y_A+y_B}, \quad Z = \frac{x_C}{x_A+x_B}, \quad Z' = \frac{y_C}{y_A+y_B},$$

x_A, x_B, and x_C are the concentrations of the primary solvent A, the extracted component B, and the extractant C in the raffinate R (% by mass) and y_A, y_B, and y_C are the concentrations of A, B, and C in the extract E (% by mass). The extract E is the solution of the extracted component B in the extractant C containing a small amount

of the component A and the raffinate R is the solution of small amounts of B and C in the primary solvent A.

Solution. Let us illustrate plotting of the triangular diagram (Fig. 35) by finding the points *6* and *6'*. First, plot the line *MN* parallel to *BC* through the point $x_A \approx 46.28$ on the line *AC*. Then plot

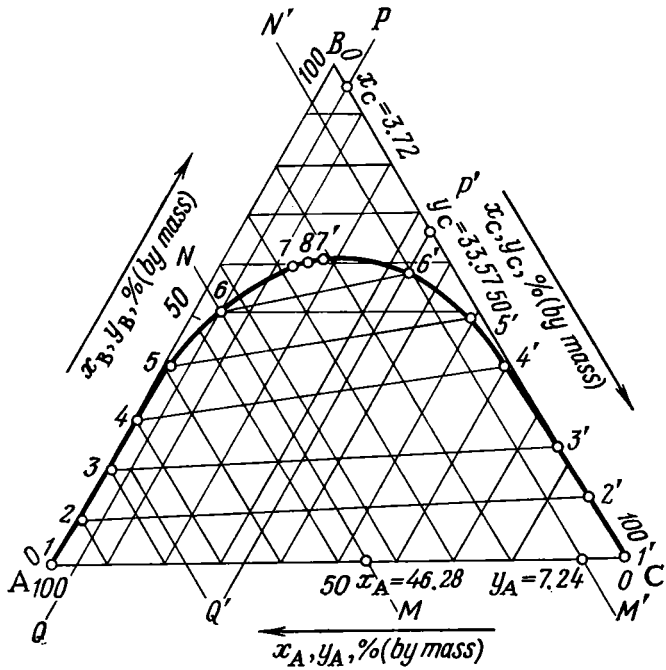


Fig. 35. The phase diagram for the system water-acetone-chlorobenzene.

the line *PQ* parallel to *AB* through the point $x_C \approx 3.72$ on the line *BC*. The intersection of the lines *MN* and *PQ* is the point *6*.

To find the point *6'* plot the line *M'N'* parallel to *BC* through the point $y_A \approx 7.24$ on the line *AC*. Then plot the line *P'Q'* parallel to *AB* through the point $y_C \approx 33.57$ on the line *BC*. The intersection of the lines *M'N'* and *P'Q'* is the point *6'*.

The other points of the diagram are plotted in a similar way and the phase diagram of the system is obtained. Passing the lines through the points *1*, *1'*; *2*, *2'*, etc. we obtain the tie lines *1-1'*; *2-2'*, etc. The point *8* is the critical point of the system.

The results of the calculations for plotting other phase diagrams are given in Table 40.

TABLE 40

Tie line	Water layer			Chlorobenzene layer		
	$x_A + x_B$	X	Z	$y_A + y_B$	Y	Z'
1-1'	99.89	0	0.0011	0.18	0	553
2-2'	99.79	0.10	0.0021	11.28	0.955	7.85
3-3'	99.69	0.20	0.0031	23.02	0.963	3.36
4-4'	99.42	0.302	0.0058	39.20	0.960	1.55
5-5'	98.64	0.407	0.0138	52.49	0.945	0.95
6-6'	96.28	0.52	0.0386	66.43	0.89	0.51
7-7'	87.41	0.69	0.144	83.92	0.73	0.18
8	86.24	0.7	0.16	86.24	0.705	0.16

The data of Table 40 are used to plot the phase diagrams in the X-Y (Fig. 36) and X-Z, Y-Z' (Fig. 37) coordinates.

The X and Z values for a given tie line describe the composition of the raffinate and the Y and Z' values describe the composition of

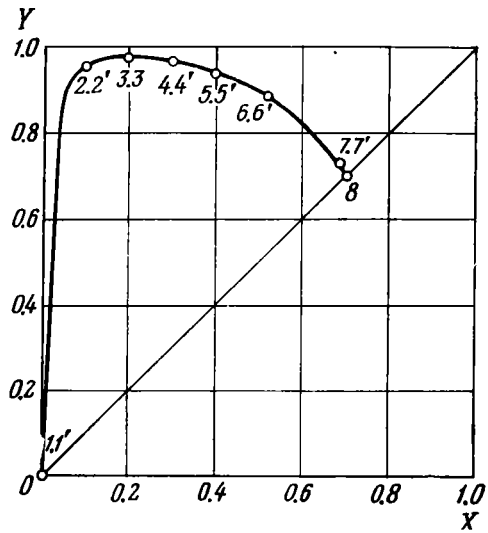


Fig. 36. The phase diagram for the system water-acetone-chlorobenzene in the X, Y coordinates.

the extract. Since the deviation of the equilibrium curve from the bisecting line passing through the origin describes the capacity of chlorobenzene to extract acetone from the acetone-water mixture it can be shown that chlorobenzene has a good extraction selectivity for this system.

Problem 30. Plot the tie line (conode) for the water-acetone-chlorobenzene mixture at the point M ($x_A = 16\%$, $x_B = 26\%$, and $x_C = 58\%$) and calculate the equilibrium phase composition.

Solution. The tie lines in the known phase diagram can be found by plotting an interpolation curve (Fig. 38) in the following way. Through the known points on the tie line pass the lines parallel to

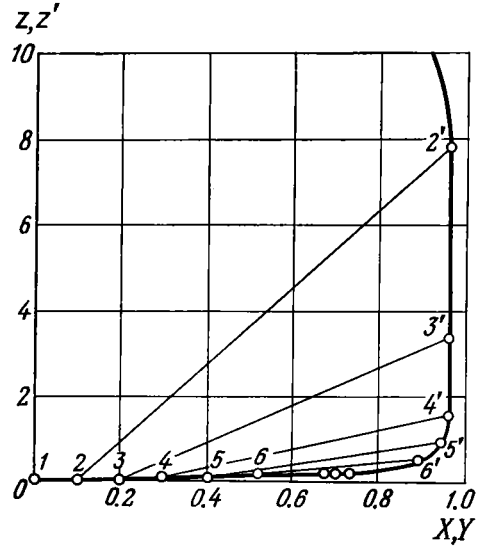


Fig. 37. The phase diagram for the water-acetone-chlorobenzene system in the X, Y; Z, Z' coordinates.

the line BC for one phase and to the line AB for the other equilibrium phase. Plot the smooth interpolation curve through the intersection points $1''$, $2''$, . . ., $6''$.

Then pass the line BM_6 through the specified point M. Plot the lines parallel to AB through the points of intersection of BM_6 with the known tie lines (M_1, M_2, . . ., M_6). Plot a smooth curve through the points of intersection between these lines and the lines passing the points 6, 5, . . ., 1 parallel to BC. The curve $8\ 6'''5'''$ . . . $1'''$ is the interpolation curve for plotting the tie lines corresponding to the points on the line BM_6. To plot the tie line for the point M plot the line parallel to AB through the point M and find its intersection K with the interpolation curve. Plot the line RK parallel to BC. The composition of the raffinate corresponds to the point R of intersection of this line with the boundary line. Find the point E of intersection of the straight line RM with the boundary curve. The line RE

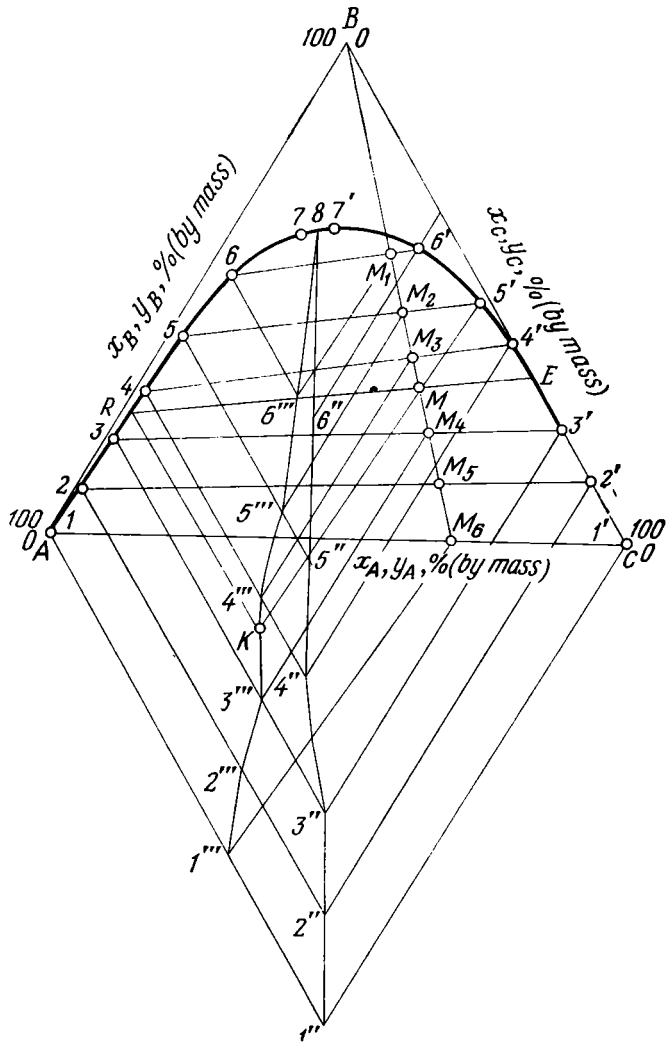


Fig. 38. Plotting of the conode (the tie line) of the phase diagram for the mixture.

is the tie line (conode) corresponding to the point M and the points R and E describe the compositions of the equilibrium phases comprising the mixture:

$$x_{A,R} = 73\%,\ x_{B,R} = 26\%,\ x_{C,R} = 1\%;\ y_{A,E} = 2\%,$$
$$y_{B,E} = 33\%,\ y_{C,E} = 65\%.$$

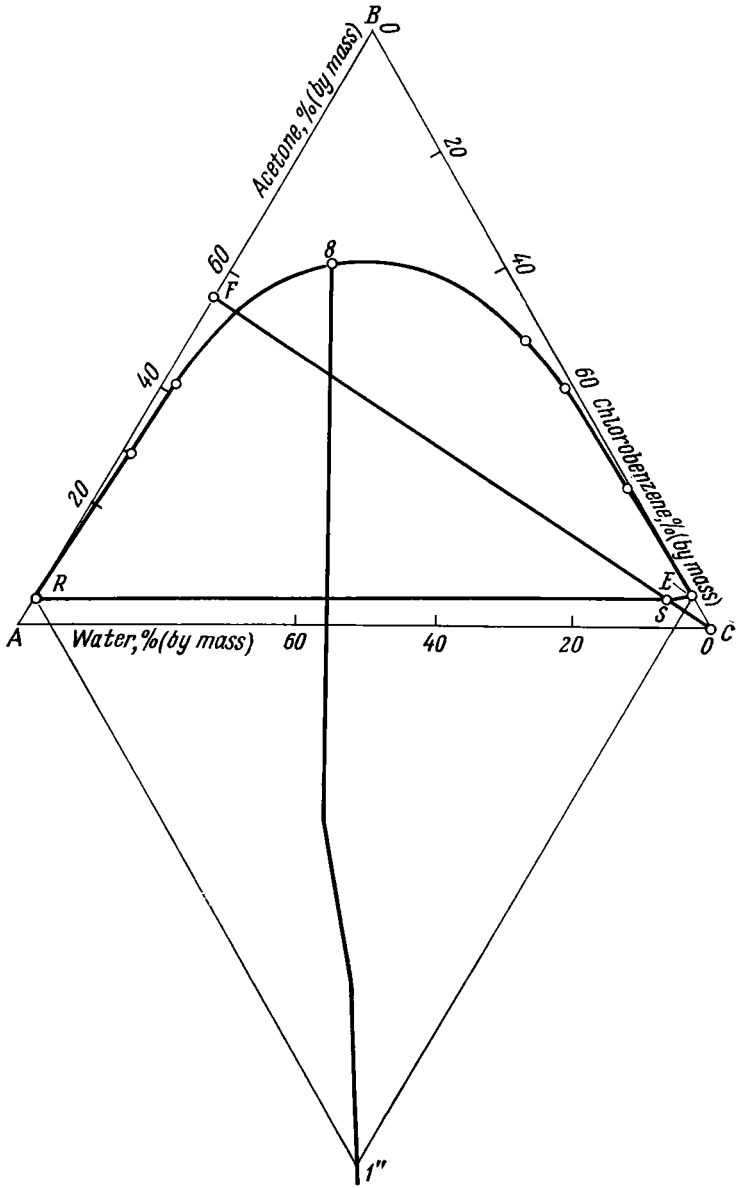


Fig. 39. The phase diagram (Problem 31).

Problem 31. Chlorobenzene (C) is used for one-stage extraction of acetone from 1000 kg of the acetone (B)-water (A) mixture containing 55% acetone. Calculate the amount of chlorobenzene required for producing raffinate containing 3.5% acetone.

Solution. We shall make use of the available phase diagram of the system (Fig. 39) and the material balance equation for the process:

$$G_F + G_C = G_E + G_R = G_S$$

Here G_F, G_C, G_E, G_R, and G_S are the amounts of the starting solution, extractant, extract, raffinate, and the mixture, respectively.

According to this equation the point S is the intersection point of the lines FC and ER. The line FC is plotted through the point C (where $x_C = 100\%$) and the point F corresponding to the starting mixture ($x_B = 55\%$ and $x_A = 45\%$).

The tie line ER is plotted through the point E on the boundary curve ($x_{B,E} = 3.5\%$) by making use of the interpolation curve *8-1"* (see Fig. 38).

Owing to the inverse proportionality we can write

$$G_S/FC = G_C/FS = G_F/SC$$

so that $G_C = G_F FS/SC$. Figure 39 yields $FS = 72$ and $SC = 9$ and we find $G_C = 1000 \times 72/9 = 8000$ kg.

Problem 32. Chlorobenzene (C) is used for extraction of acetone from 1000 kg of the acetone (B)-water (A) mixture containing 55% acetone. The raffinate should contain 3.5% acetone. Calculate the number of the theoretical stages, the compositions and amounts of the products at each stage for cross-current feeding of 200 kg of pure chlorobenzene at each stage and for counter-current feeding of extractant if 664 kg of pure chlorobenzene are fed at the last stage.

Solution. Figure 40 presents the diagram of the multistage extraction process with cross-current and counter-current flow of the extractant. Calculations will be made on the basis of the phase diagram for the system and the material balance equations.

The material balance equation for the ith stage can be written as

$$G_C + G_{R,\,i-1} = G_{R,\,i} + G_{E,\,i} = G_{S,\,i}; \quad i = 1,\ 2,\ \ldots,\ n$$

where G_C is the amount of the extractant (kg); $G_{R,i}$, $G_{E,i}$, and $G_{S,i}$ are the amounts of the raffinate, extract, and mixture discharged from the ith stage (kg); and n is the theoretical number of the extraction stages.

The problem may be solved with a graphical technique (see Fig. 41). When $i = 1$ we obtain

$$G_C + G_{R,\,0} = G_{R,\,1} + G_{E,\,1} = G_{S,\,1}$$

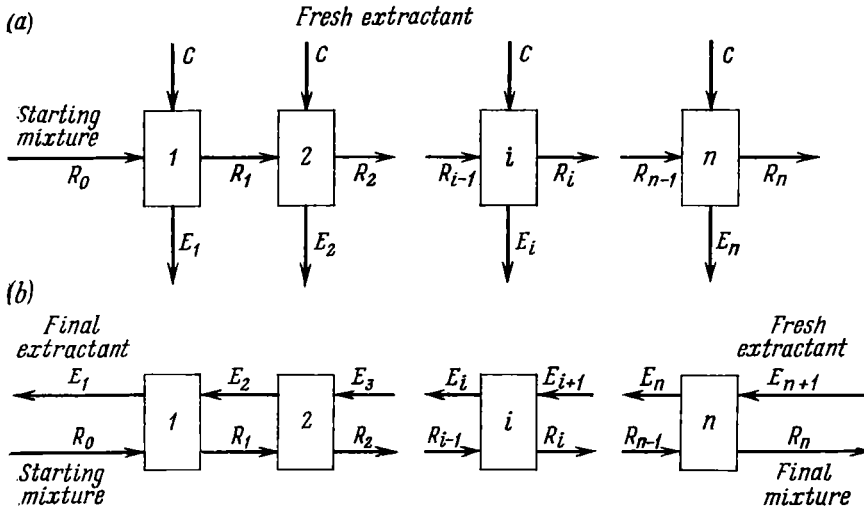
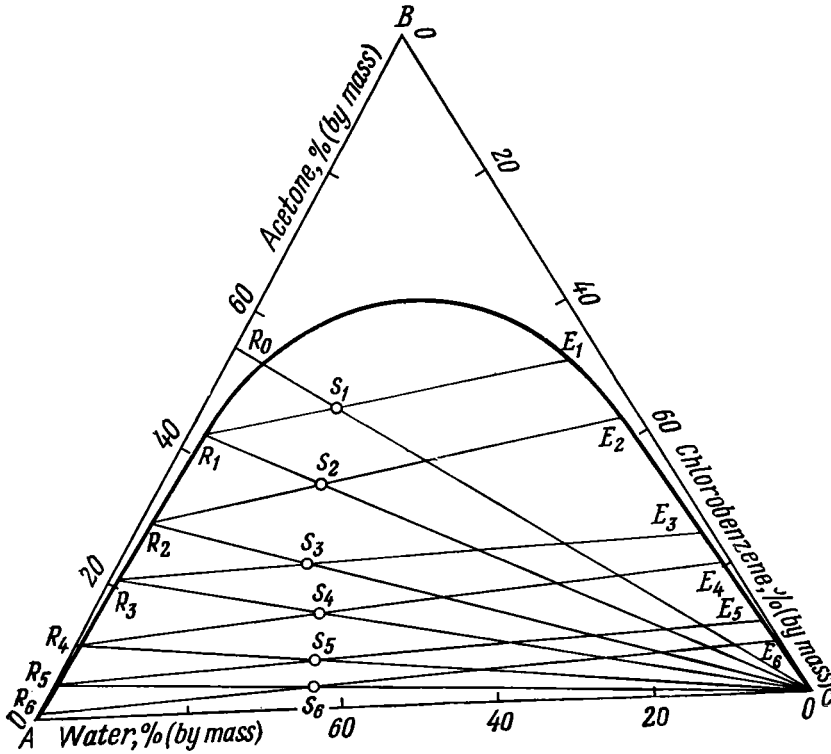


Fig. 40. Multistage liquid-liquid extraction with cross-current (a) and countercurrent (b) flow of the extractant.



41. Diagram for calculation of the cocurrent extraction.

Hence, the point S_1 describing the composition of the mixture at the stage 1 is the intersection of the lines CR_0 and R_1E_1. The inverse proportionality yields, furthermore, $G_{R,0}R_0S_1 = G_CS_1C$ or $G_{R,0}R_0S_1 = G_C(R_0C - R_0S_1)$ since it is seen that $S_1C = R_0C - R_0S_1$. To find R_0C plot the line through the point C (where $x_C = 100\%$) and the point R_0 (where $x_B = 55\%$) and obtain $R_0C = 78$ mm.

The position of the point S_1 can be found from the following equation:

$$R_0S_1 = \frac{R_0C}{1+\frac{G_{R,0}}{G_C}} = \frac{78}{1+\frac{1000}{200}} = 13 \text{ mm}$$

Since raffinate and extract are at equilibrium and the point S_1 should be on the tie line E_1R_1 we have to plot the tie line passing through the point S_1 as described in Problem 31. Using this tie line we can determine the compositions of raffinate and extract (the points R_1 and E_1) discharged from the first stage and fed to the second stage:

$$x_{A,R1} = 56,\ x_{B,R1} = 42,\ x_{C,R1} = 2,\ y_{A,E1} = 5,\ y_{B,E1} = 53,$$

$$y_{C,E1} = 42$$

To find the amounts of extract and raffinate after the first stage we can use the inverse proportionality relationships and obtain

$$G_{S,1} = G_{R,0} + G_C = 1000 + 200 = 1200 \text{ kg}$$

$$G_{R,1} = G_{S,1}\frac{E_1S_1}{E_1R_1} = 1200 \times 28/43.5 = 776 \text{ kg}$$

$$G_{E,1} = G_{S,1} - G_{R,1} = 1200 - 776 = 424 \text{ kg}$$

Let us now make calculations for the second stage of absorption. The material balance equation can be written as

$$G_C + G_{R,1} = G_{R,2} + G_{E,2} = G_{S,2}$$

The lines R_1C and R_2E_2 intersect at the point S_2. As above we obtain

$$R_1S_2 = \frac{R_1C}{1+\frac{G_{R,1}}{G_C}}$$

From Fig. 41 we find $R_1C = 76$ mm. Then $R_1S_2 = 15.6$ mm. Then we plot the tie line R_2E_2 passing through the point S_2 and find $x_{A,R2} = 70$, $x_{B,R2} = 29$, $x_{C,R2} = 1$, $y_{A,E2} = 2$, $y_{B,E2} = 43$, $y_{C,E2} = 55$.

Similar calculations can be made for $i = 3, 4, 5, 6$. The results are given in Table 41.

TABLE 41

Stage number i	Raffinate				Extract			
	Amount, kg	x_A, %	x_B, %	x_C, %	Amount, kg	y_A, %	y_B, %	y_C, %
1	776	56	42	2	424	5	53	42
2	620	70	29	1	356	2	43	55
3	550	78	21	1	270	1	25.5	73.5
4	464	89	10.5	0.5	286	1	20	79
5	410	95.5	4.2	0.3	254	0.2	12	87.8
6	378	99	1	0	232	0	8	92

For any i the following equations are satisfied:

$$R_{i-1}S_i = \frac{R_{i-1}C}{1+\frac{G_{R,\,i-1}}{G_C}}, \quad G_{R,\,i} = G_{S,\,i}\,\frac{E_iS_i}{E_iR_i},$$

$$G_{S,\,i} = G_{R,\,i-1} + G_C, \quad \text{and} \quad G_{E,\,i} = G_{S,\,i} - G_{R,\,i}$$

The data of Table 41 show that the number of extraction stages needed to reduce the acetone concentration in raffinate to about 3.5% is 5-6 and the respective total amount of the extractant is 1000-1200 kg. The total amount of the extract at all the six stages is $G_E = 1822$ kg.

The concentration of the components in the mixture of the extracts can be found from the material balance equations for the components A, B, and C:

$$y_{A,\,E}G_E + G_{R,\,6}x_{A,\,R6} = G_{R,\,0}x_{A,\,R0}$$

$$y_{B,\,E}G_E + G_{R,\,6}x_{B,\,R6} = G_{R,\,0}x_{B,\,R0}$$

$$y_{C,\,E} = 100 - y_{A,\,E} - y_{B,\,E}$$

Hence, we obtain $y_{A,E} = 4.1$, $y_{B,E} = 30.2$, and $y_{C,E} = 65.7$.

Let us now analyse the counter-current extraction process (Fig. 40*b*). The material balance equation for the ith stage is

$$G_{E,\,i+1} - G_{R,\,i} = G_{E,\,1} - G_{R,\,0} = G_{E,\,n+1} - G_{R,\,n} = G_S$$

or

$$G_{E,\,n+1} + G_{R,\,0} = G_{E,\,1} + G_{R,\,n} = G_S, \quad i = 1,\ 2,\ \ldots,\ n$$

The last equation shows that the mixtures corresponding to the points E_{n+1} and R_0 on one hand and E_1 and R_n on the other hand has the same composition corresponding to the point S and the amount of such a mixture is G_S (Fig. 42).

Hence, the point S should be the point of intersection of the straight lines $E_{n+1}R_0$ and R_nE_1. The line $E_{n+1}R_0$ is plotted through

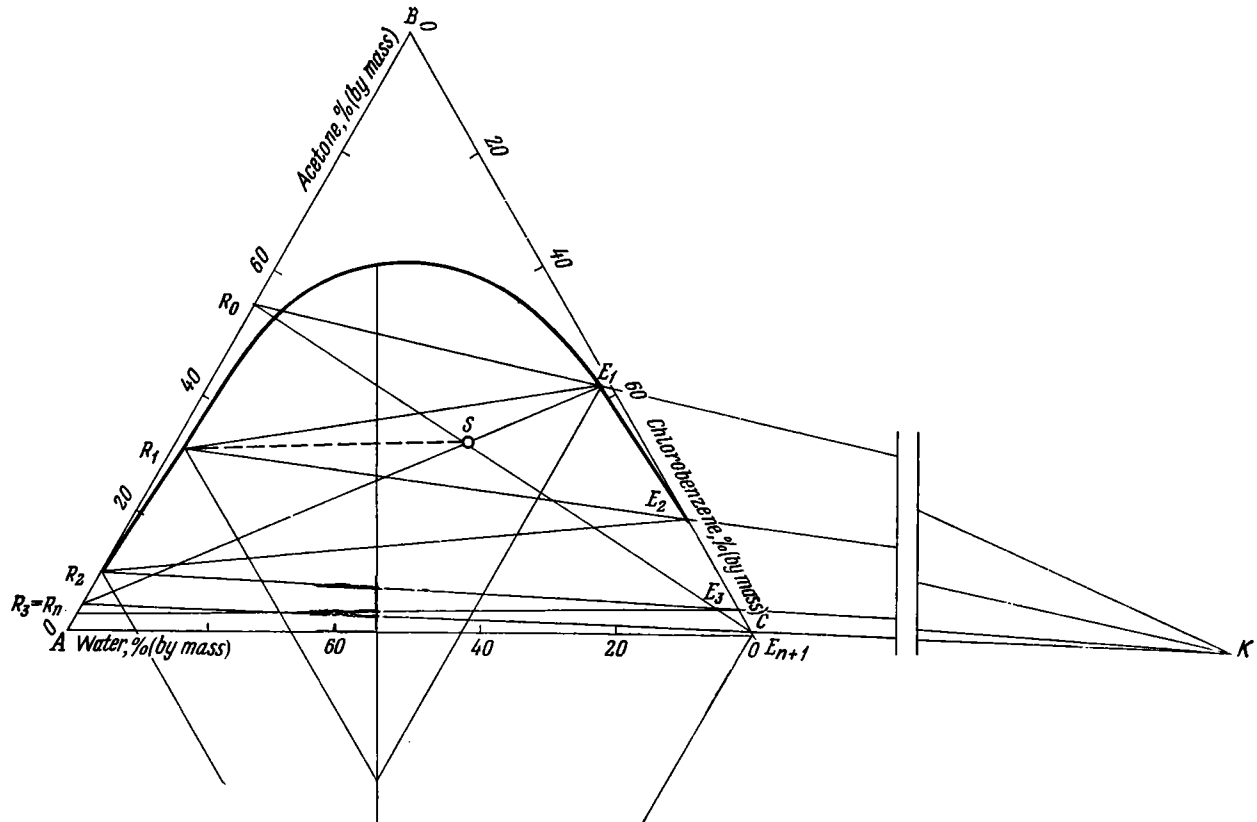


Fig. 42. Diagram for calculation of counter-current extraction.

the point E_{n+1} corresponding to the pure extractant and the point R_0 corresponding to the starting mixture. From the inverse proportionality it follows that the point S is on the line $E_{n+1}R_0$ and

$$G_{R,\,0}R_0S = G_{E,\,n+1}SE_{n+1}$$

Since we have

$$R_0S + SE_{n+1} = R_0E_{n+1}$$

we obtain

$$G_{R,\,0}R_0S = G_{E,\,n+1}(R_0E_{n+1} - R_0S)$$

and

$$R_0S = R_0E_{n+1}/(1 + G_{R,\,0}/G_{E,\,n+1})$$

From Fig. 42 we obtain $R_0E_{n+1} = 88$ mm so that $R_0S = 38$ mm.

Since the point S also belongs to the line R_nE_1 the line passing through the points R_n and S intersects the boundary curve at the point E_1. Plot the tie line through the point E_1 and find the point R_1. The points E_1 and R_1 describe the composition of raffinate and extract in the first absorption stage: $x_{A,R1} = 68$, $x_{B,R1} = 30$, $x_{C,R1} = 2$, $y_{A,E1} = 1$, $y_{B,E1} = 42$, $y_{C,E1} = 57$.

The amount of the extract at the first stage is

$$G_{E,\,1} = G_S R_nS/R_nE_1$$

From Fig. 42 we find $R_nS = 61$ mm and $R_nE_1 = 83$ mm so that $G_{E,1} = (1000 + 760)\,61/83 = 1300$ kg.

The amount of raffinate at the nth stage is $G_{R,n} = 1760 - 1300 = 460$ kg.

Now we shall make use of the plot for equation

$$G_K + G_{R,\,i} = G_{E,\,i+1}$$

First we have to find the point K. Since we have $G_{R,n} + G_K = G_{E,n+1}$ the point K should be on the line R_nE_{n+1} and since $G_{R,0} + G_K = G_{E,1}$ the point K should be also on the line R_0E_1. Thus, the point K is the point of intersection of the lines R_nE_{n+1} and R_0E_1 (Fig. 42).

The composition of the extract at the first stage is given by E_2 which is the point of intersection of the line KR_1 and the right branch of the boundary curve. The point R_2 describing the composition of raffinate is found as the point of intersection of the boundary curve with the tie line passing through the point E_2.

Similar calculations for other stages yield the results summarized in Table 42.

The amounts of raffinate and extract at the ith stage can be found from the following equations derived from the material balance equations:

$$G_{R,\,i} = \frac{G_{R,\,i-1}(x_{B,\,R_{i-1}} - y_{B,\,E_{i+1}}) + G_{E,\,i}(y_{B,\,E_{i+1}} - y_{B,\,E_i})}{x_{B,\,R_i} - y_{B,\,E_{i+1}}} \qquad \text{(VII.107)}$$

TABLE 42

Stage, i	Raffinate				Extract			
	Amount, kg	x_A, %	x_B, %	x_C, %	Amount, kg	y_A, %	y_B, %	y_C, %
1	590	68	30	2	1300	1	42	57
2	380	90	10	0	890	0.5	19.5	80
3	460	97	3	0	680	0	5	95

$$G_K = G_{E,1} - G_{R,0} \quad \text{and} \quad G_{E,i+1} = G_K + G_{R,i}$$

For instance, for $i = 1$ we obtain

$$G_{R,1} = \frac{G_{R,0}(x_{B,R0} - y_{B,E2}) + G_{E,1}(y_{B,E2} - y_{B,E1})}{x_{BR1} - y_{BE2}} = 590 \text{ kg} \quad \text{(VII.108)}$$

$$G_K = 1300 - 1000 = 300 \text{ kg} \quad \text{and} \quad G_{E,1} = 300 + 590 = 890 \text{ kg}$$

Problem 33. The activated carbon (0.45 kg) is used to adsorb benzene from 1200 litres of the gas mixture containing 5% (by volume) of benzene at 20 °C. Benzene is desorbed from the activated carbon by superheated steam at 200 °C. Calculate the benzene content in the gas mixture after adsorption and the degree of utilization of benzene.

Solution. The adsorption capacity of activated carbon at 20 °C is 0.382 g and at 200 °C 0.0696 g of benzene per 1 g of carbon.

The amount of benzene adsorbed by 0.45 kg of activated carbon at 20 °C is $0.382 \times 450 = 172$ g or $172 \times 22.4 \times 293/78 \times 273 = 53$ litres.

The amount of benzene remaining in the gas mixture after adsorption is $1200 \times 0.05 - 53 = 7$ litres so that the benzene concentration in the mixture after adsorption is $7 \times 100/(1200 - 53) = 0.61\%$.

The amount of benzene remaining in activated carbon after desorption with steam is $0.0696 \times 450 = 31.5$ g or 9.7 litres (at 20 °C). Thus, $53 - 9.7 = 43.3$ litres of benzene are desorbed. The degree of utilization of benzene is $43.3 \times 100/83 = 81.6\%$.

Problem 34. Plot the isotherm of adsorption of diethyl ether by activated carbon at 293 K using the isotherm of adsorption of benzene by this activated carbon at 293 K (Fig. 43). Given below are the points on the isotherm of adsorption of benzene by activated carbon at 293 K.

P, 10^3 Pa	0.133	0.332	1.330	2.660	3.990	5.320	6.650	7.980	9.250
G_1, kg of benzene per kg of carbon	0.150	0.200	0.260	0.280	0.288	0.292	0.297	0.302	0.304

The saturated vapour pressure of diethyl ether at 293 K is $p_{sat_2} = 59 \times 10^3$ Pa. The density of diethyl ether at 293 K is 714 kg/m³. Molecular masses: benzene—78, diethyl ether—74.

Solution. The molar volume of diethyl ether is $V_2 = 74/714 = 0.104$ m³/kmole. The affinity coefficient is $\beta = 0.104/0.089 = 1.17$. Equation (VII.13) yields the formulas for calculating the points on the isotherm for diethyl ether:

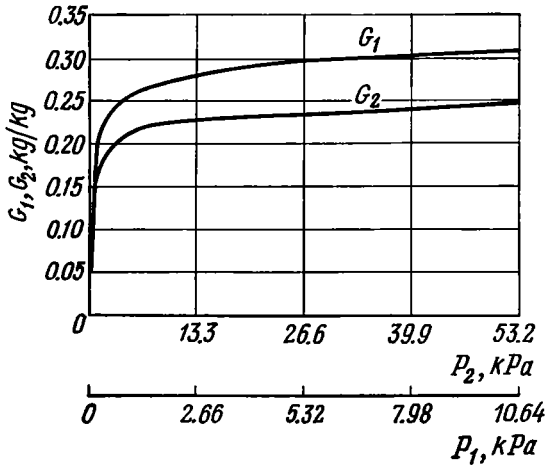


Fig. 43. Isotherm for adsorption of benzene and diethyl ether at 293 K.

$$\ln P_2 = \ln 59 - 1.17 \frac{293}{293} \ln \frac{10}{P_1}$$

$$G_2 = \frac{G_1}{78} \frac{0.089}{0.104} 74 \text{ kg of ether/kg of carbon}$$

or

$$P_2 = \exp (4.08 - 1.17 \ln (10/P_1)) \text{ and } G_2 = 0.81 G_1.$$

The calculation results for the isotherm of adsorption of diethyl ether by activated carbon at 293 K are given below.

P_2, 10^3 Pa	0.39	1.10	5.60	12.50	20.00	28.00	36.70	45.00	54.00
G_2, kg of ether per kg of carbon	0.121	0.162	0.210	0.226	0.233	0.237	0.240	0.244	0.246

These results are used to plot the adsorption isotherm for diethyl ether at 293 K.

Problem 35. Calculate the time of adsorption of the ethanol and diethyl ether vapour from the air at 293 K. The initial concentration

of the vapour in the air-vapour mixture is $C_1 = 1.08$ kg/m³, the final concentration of the vapour in the mixture discharged from the apparatus is $C_f = 0.0054$ kg/m³. The velocity of the vapour-air mixture is $w = 0.167$ m/s. The height of the adsorbent layer is $H = 0.6$ m. The mean diameter of the activated carbon pellet is $d_m = 0.004$ m. The bulk density of the activated carbon is 500 kg/m³. The kinematic viscosity of the vapour-air mixture is $\nu = 0.16 \times \times 10^{-4}$ m²/s. The diffusion coefficient for the mixture is $D = 0.083 \times 10^{-4}$ m²/s at 293 K.

Solution. The adsorption process can be described by the following system of equations:

$$\begin{cases} \partial C/\partial \tau = -w \dfrac{\partial C}{\partial x} - \dfrac{\partial G}{\partial \tau} \\ \partial G/\partial \tau = K(C - C^*) \\ G = f(C^*) \end{cases} \qquad \text{(VII.109)}$$

for $x = 0$ $C = C_0$; for $\tau = 0$ $C = 0$, $G = 0$.

Here C is the concentration of the adsorbed component in the gas mixture (kg/m³), w is the velocity of the gas along the axis x, and τ is the time of adsorption.

We can make use of an approximation technique for determination of the time of adsorption τ_f from the known isotherm of adsorption of diethyl ether (see Fig. 43). Since the initial vapour concentration in the gas mixture is 1.08 kg/m³ its initial partial pressure is

$$p_1 = C_1 RT = 1.08 \times 0.0821 \times 293 \times 101.3/74 = \\ = 35.5 \times 10^3 \text{ Pa}$$

From the adsorption isotherm we find $G_1 = 0.24$ kg of ether per 1 kg of carbon $= 0.24 \times 500 = 120$ kg of ether per 1 m³ of carbon. For benzene we obtain $G = 0.24 \times 78/74 = 0.253$ kg per 1 kg of carbon. The isotherm of benzene adsorption (Fig. 43) yields the respective partial pressure of benzene $p = 2.12 \times 10^3$ Pa.

Since we have $p/p_{sat} = 2.12/10 > 0.17$ the duration of adsorption can be found from the following formula:

$$\sqrt{\tau_f} = \sqrt{\frac{G_1 H}{wC_1}} - b\sqrt{\frac{G_1}{KC_1}} \qquad \text{(VII.110)}$$

Here $b = f(C_f/C_1)$. For our process $C_f/C_1 = 5 \times 10^{-3}$ and $b = 1.84$.

The mass transfer coefficient is given by

$$K = \frac{1.6 D w^{0.54}}{\nu^{0.54} d_m^{1.46}} \qquad \text{(VII.111)}$$

For the conditions of this process Eq. (VII.111) yields $K = = 6.05$ s⁻¹. We obtain from Eq. (VII.110) $\tau_f = 224$ s.

Problem 36. The vapour-air mixture with the initial concentration of the vapour $C_1 = 0.1$ kg/m³ is fed into an adsorption column with the velocity 0.5 m/s. The vapour concentration in the discharged gas is $C_f = 0.006$ kg/m³. The vapour is adsorbed by activated carbon continuously fed into the column. The isotherm of adsorption of the

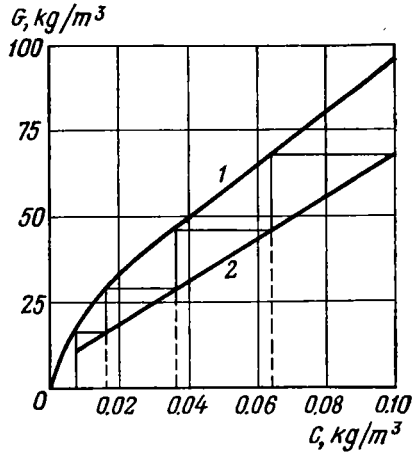


Fig. 44. The adsorption isotherm (*1*) and the actual adsorption plot (*2*)

component is given in Fig. 44. The mass transfer coefficient for the process is $K = 6$ s^{-1}. Activated carbon is discharged from the column at 70% saturation. Calculate the height of the activated carbon layer and its velocity in the column.

Solution. The amount of the adsorbed component corresponding to $C_1 = 0.1$ kg/m³ can be found from the isotherm in Fig. 44: $G_1 = 68$ kg/m³. Since the activated carbon adsorbs the component only to 70% of its capacity we obtain $G_1 = 68 \times 0.7 = 47.6$ kg/m³.

The velocity of the adsorbent layer is given by the equation derived in the monograph [34]:

$$w_a = C_1 w / G_1 = 0.1 \times 0.5/47.6 = 0.105 \times 10^{-2} \text{ m/s}^{-1}$$

The height of the adsorbent layer is

$$H = wm/K \qquad \text{(VII.112)}$$

where m is the total number of the transfer units. The height H can be calculated in two ways.

1. Plot a stepwise line between the adsorption isotherm (curve *1*) and the actual adsorption plot (curve *2*) in Fig. 44. From the point on the curve *2* corresponding to C_1 plot a straight line parallel to the horizontal axis and find the point of its intersection with the adsorption isotherm. Starting from this point continue plotting until we

reach a point on curve *2* which approximately corresponds to C_t. The number of steps is $n = 4$.
Here we have

$$m = \sum_{j=1}^{n} m_j \qquad \text{(VII.113)}$$

where n is the number of steps of concentration variation and m_j is the number of the transfer units at the jth step:

$$m_j = \frac{2(C_{j-1} - C_j)}{C_{j-1} - C_{j+1}}, \quad j = 1, 2, \ldots, n$$

From Fig. 44 we obtain the following results for each step:

$$m_1 = 2(0.1 - 0.065)/(0.1 - 0.037) = 1.11$$
$$m_2 = 2(0.065 - 0.037)/(0.065 - 0.016) = 1.14$$
$$m_3 = 2(0.037 - 0.016)/(0.037 - 0.006) = 1.35$$
$$m_4 = 2(0.016 - 0.006)/(0.016 - 0.003) = 1.54$$
$$\sum_{j=1}^{4} m_j = 5.14$$

Equation (VII.112) yields $H = 0.5 \times 5.14/6 = 0.43$ m.

2. The total number of the transfer units can be found from the following equation:

$$m = \int_{C_t}^{C_1} \frac{dC}{C - Y} \qquad \text{(VII.114)}$$

where Y is the equilibrium concentration.

Given below are the results of preliminary calculations obtained from the adsorption isotherm in Fig. 44.

C	0.006	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
$C-Y$	0.003	0.006	0.012	0.018	0.022	0.025	0.027	0.029	0.031	0.035
$1/(C-Y)$	333	167	83.5	55.5	45.5	40	37	34.5	32.3	28.6

These results are used to plot $(C - Y)^{-1}$ as a function of C (Fig. 45) for graphical integration of Eq. (VII.114). We obtain $m = 0.01 \times \times 120 + 0.01 \times 48 + 0.01 \times 68 + 0.01 \times 42 + 0.01 \times 38 + + 0.01 \times 34 + 0.01 \times 32 + 0.02 \times 30 + 0.004 \times 216 = 5.28$. Hence we find from Eq. (VII.112) $H = 0.5 \times 5.28/6 = 0.44$ m.

Problem 37. Calculate the mean size of crystals grown in the cascade of three crystallizers. The linear velocity of growth in all crystallizers is $\lambda = 1.5 \times 10^{-7}$ m/s. The measured numbers of crystals formed in the cascade are $w_1 = 1 \times 10^{12}$ in the first crystallizer, $w_2 = 2 \times 10^{12}$ in the second crystallizer, and $w_3 = 4 \times 10^{12}$ in

the third crystallizer. The crystallizer volume is $V = 2$ m³. The flow rate of the crystallization solution is $L = 20$ m³/h.

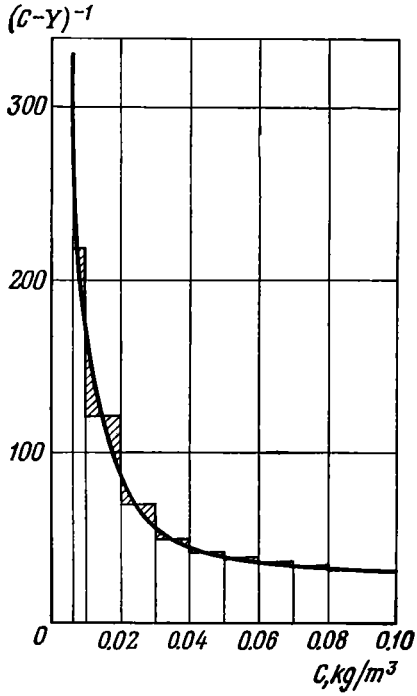


Fig. 45. Determination of the total number of transfer units by graphical integration.

Solution. The size distribution of the crystals is described by the following function:

$$\varphi(l) = \exp(-l/\lambda\tau) \sum_{j=1}^{i} w_j \frac{l^{i-j}}{(\lambda\tau)^{i-j}(i-j)!} \qquad \text{(VII.115)}$$

Here l is the linear size of crystals, τ is the time of residence of crystals in the crystallizer, w_j is the number of crystals formed in the jth crystallizer, and i is the number of crystallizers in the cascade.

The mean size l_m of the crystals can be found as

$$l_m = \frac{\int_{j=1}^{i} l\varphi(l)\,dl}{\int_{j=1}^{i} \varphi(l)\,dl} = \lambda\tau \frac{\sum_{j=1}^{i} w_j (i-j+1)}{\sum_{j=1}^{i} w_j} \qquad \text{(VII.116)}$$

The time of residence of crystals in the crystallizer is $\tau = V/L = 2/20 = 0.1$ h.

For the cascade of three crystallizers ($i = 3$) Eq. (VII.116) yields $l_m = 0.085$ mm.

Further Problems for Students

1. Calculate the amount of oxygen from the air dissolved in 25 kg of water under the pressure of 15×10^6 Pa at 20 °C.
2. Calculate the equilibrium composition of the gas over the liquid mixture containing 25% benzene, 35% toluene, and 40% *o*-xylene at 100 °C (find the vapour pressures for pure components in reference sources).
3. Calculate the vapour pressure over the water containing 19% (by mass) of glycerol at 22 °C.
4. Ammonia from a gas mixture is absorbed by water in a froth apparatus. Calculate the driving force of absorption for the counter-current and cross-current conditions. The pressure is 10^5 Pa, the temperature is 20 °C. The ammonia concentration in the gas mixture is reduced from 6% to 0.9% (by volume) and the ammonia concentration in water increases from 0.06 kmole/m³ to 0.3 kmole/m³.
5. Calculate the degree of extraction of ammonia for the conditions of Problem 5.
6. Calculate the driving force of absorption and the efficiency of the direct flow scrubber with packing for absorption of nitrogen oxides with a $3N$ soda solution. The temperature is 30 °C, the pressure is 10^5 Pa. The starting concentration of nitrogen oxides (calculated for N_2O_3) is 1% and the final concentration is 0.1% (by volume).
7. Calculate the diffusion coefficient of sulphur dioxide in the air at 18 °C under the pressure of 10^5 Pa.
8. Calculate the diffusion coefficient of sulphur dioxide in the water at 18 °C.
9. Find the effective diffusion coefficient of benzene for benzene absorption by the coal-tar oil in the froth apparatus at 250 °C. The gas velocity in the apparatus is 2.1 m/s, the irrigation density is 6 m³/m² h and the height of the starting layer of oil is 25 mm.
10. Calculate the mean time of residence of the reactants in the reactor from the measured concentrations of the discharged indicator given below:

τ, s	0	10	20	30	40	50	60	70	80	90	100
C, kmole/litre	0	1	2	12	14	11	7	4	1	0	0

11. Using the data of Problem 10 calculate the degree of conversion in the irreversible reaction of the first order if the reaction rate constant is 0.147 s^{-1}.
12. Calculate the consumption of sulphuric acid for drying air under the atmospheric pressure in the column with packing under the counter-current conditions. The initial moisture content in the air is 0.03 kg per 1 kg of dry air, the final moisture content is 0.005 kg per 1 kg of dry air. The initial concentration of water in the acid is 0.5 kg per 1 kg of monohydrate and the final concentration is 1.4 kg per 1 kg of monohydrate.

13. Calculate the mass-transfer coefficient for absorption of carbon dioxide in a water scrubber. The gas flow rate is 5000 m^3/h, the water flow rate is 650 m^3/h. The initial concentration of carbon dioxide in the gas is 28.4% (by volume), the final concentration (at the top of the scrubber) is 0.2% (by volume). The pressure is 16.5×10^5 Pa, the temperature is 15 °C. The lower part of the scrubber contains 6000 $75 \times 75 \times 2$ mm packing rings and the upper part contains 320 000 $50 \times 50 \times 1.5$ mm rings.

14. Calculate the mass-transfer coefficient for absorption of acetone from the air by water in a packed spray tower. The water flow rate is 4000 kg/h. The flow rate of pure air is 2000 m^3/h and the gas mixture contains 5% (by volume) of acetone vapour. The degree of absorption of acetone at 20 °C is 98.2%. The absorption tower is packed with ceramic $25 \times 25 \times 3$ mm rings to the height of 18 m. The gas velocity in the tower is 20% less than the velocity corresponding to the beginning of emulsification.

15. Chlorine is absorbed by milk of lime in a multi-bed froth absorber under the counter-current conditions. The milk of lime contains 100 g of CaO per 1 litre. Calculate the mean driving force of absorption providing for 95% degree of absorption of chlorine.

16. Calculate the mass-transfer coefficient for the process described in Problem 15. The gas velocity in the apparatus is 2 m/s, the froth height at each bed is 200 mm. Find also the number of beds in the apparatus. Use the equations for absorption of highly soluble gases.

17. From the nomogram in Fig. 30 find the efficiency for one bed of the froth apparatus for desorption of ammonia from weak ammonia liquor by live steam. The consumption of steam is 0.3 kg per 1 kg of the liquid, the height of the froth layer is 0.18 m, the pressure is 1.01×10^5 Pa.

18. Calculate the size of the column for absorption of a component of a gas mixture which enters into reaction with the absorbent if the required area of the absorption surface is 3000 m^2. The absorbent viscosity is 10^{-3} Pa s, the density of the gas mixture is 0.65 kg/m^3, the density of the liquid absorbent is 1000 kg/m^3, the flow rate of the absorbent is 16 000 kg/h, the flow rate of the gas mixture is 6500 m^3/h (at the temperature and pressure of the process).

19. The following experimental results were obtained for a mass-exchange process [3]:

	Gas	Liquid
Re value	500	50
Pr value	0.74	13.9
Irrigation density L, kmole/m^2 h	146	73
Concentration of the non-diffusing liquid component, kmole/m^3	—	25.6
Partial pressure of the non-diffusing gas component, 10^6 Pa	0.09	—

The Henry's law constant is 625 Pa/kmole m³. Find the mass-transfer coefficients k_g and k_l for the gas and the liquid and the overall mass-transfer coefficient.

20. Given below are the experimental results obtained for the system described in Problem 19 for Re = 500 and Pr′ = 0.84.

t, °C	38	93	149	38	38
L, kmole/h	13.6	13.6	13.6	4.54	31.7
D, m²/h	0.066	0.0845	0.103	—	—
μ, Pa s	0.0185	0.0208	0.0230	—	—
ρ_g, kg/m³	1.20	1.008	0.88	—	—

In all experiments the partial pressure of the non-diffusing gas component was 0.09×10^6 Pa. Calculate the mass-transfer coefficient for each experiment.

21. Plot the phase diagrams in the coordinates X, Y-Z, Z and X-Y (see Chapter VII, Problem 29) for the system water (A)-acetic acid (B)-diisopropyl ether (C) at 20 °C using the data of Table 43.

TABLE 43

Composition of the water layer, % by mass			Composition of the ether layer, % by mass		
A	B	C	A	B	C
98.1	7.70	1.2	0.5	0.20	99.3
97.1	1.40	1.5	0.7	0.40	98.9
95.5	2.90	1.6	0.8	0.80	98.4
91.7	6.40	1.9	1.0	1.90	97.1
84.4	13.30	2.3	1.9	4.80	93.3
71.1	25.50	3.1	3.9	11.40	84.7
58.9	36.70	4.4	6.9	21.00	71.5
45.1	44.30	10.6	10.8	31.10	58.1
37.1	46.40	16.5	15.1	36.20	48.7

22. Plot the boundary curve and the tie lines in the triangular phase diagram for the system and conditions of Problem 21.

23. Plot the tie line corresponding to the raffinate composition $x_{A,R1} = 49\%$, $x_{B,R1} = 42\%$, and $x_{C,R1} = 9\%$ for the conditions of Problem 21. Calculate the equilibrium amounts of the phases (R_1 and E_1) if the total amount of the mixture is 200 kg and the amount of acetic acid is 80 kg.

24. Diisopropyl ether is used to extract acetic acid from 1000 kg of 60% aqueous solution of acetic acid producing raffinate containing 10% acetic acid. Calculate the theoretical number of extraction stages

for direct flow extraction with 250 kg of pure diisopropyl ether consumed at each stage. Make use of the data in Table 43.

25. Diisopropyl ether is used for multi-stage counter-current extraction of acetic acid from 60% aqueous solution of acetic acid producing raffinate containing 5% acetic acid. The flow rate of the starting solution is 1000 kg/h and the flow rate of the extractant is 500 kg/h. Calculate the theoretical number of extraction stages and the consumptions and compositions of the products at each of the stages.

26. 200 m^3 of the air-vapour mixture containing 0.006 kg/m^3 of diethyl ether are fed into a batch-process adsorber at the temperature 20 °C and the atmospheric pressure. The velocity of the gas mixture is 13 m/min. The final concentration of diethyl ether in the gas mixture is 3×10^{-5} kg/m^3. The adsorbent is the activated carbon with the bulk density 500 kg/m^3. The effective diameter of the carbon pellets is 0.004 m, the height of the adsorbent layer is 0.7 m. Using the adsorption isotherm for benzene at 20 °C (Fig. 43) plot the isotherm for adsorption of diethyl ether from the air at 20 °C. From this isotherm calculate the amount of the activated carbon needed for one batch, the apparatus diameter, and the duration of the process.

Chapter VIII

Electrochemical Processes

Introduction

The processes which involve transformations of electric energy into the chemical energy or vice versa are known as the electrochemical processes.

The electrochemical processes are governed by the Faraday laws. According to the first Faraday law in any electrode process the amount of material converted by electrolysis is proportional to the current and the time of its passage, that is, the total electric charge passed.

The second Faraday law describes the effect of the nature of ions. According to it the amounts of different substances converted by passage of the same electric charge are proportional to their equivalent masses. The electric charge required to liberate 1 equivalent of any substance by electrolysis is 96 500 coulombs or 26.8 A h.

Owing to the secondary processes the amount of the substance liberated by electrolysis is always smaller than that specified by the Faraday law.

The efficiency of electric energy utilization in electrolytic processes is basically characterized by the yield by current (in percentages) and the coefficient of energy utilization. The yield by current η is the ratio of the actual amount G_a of material obtained by electrolysis to the amount G_{max} which should be obtained with the same energy consumption according to the Faraday law:

$$\eta = \frac{G_a}{G_{max}} 100\% \qquad \text{(VIII.1)}$$

The concept of the yield by current is similar to the concept of the product yield in chemical processes. From the Faraday law we obtain

$$G_{max} = \frac{I\tau E}{1000} \qquad \text{(VIII.2)}$$

where I is the current (A), τ is the duration of electrolysis (h), and E is the amount of material liberated at the electrode with passage of the charge of 1 A h.

The coefficient of energy utilization μ (in percentages) is the ratio of the theoretically required energy W_{th} to the actual amount of energy W_a consumed with electrolysis:

$$\mu = \frac{W_{th}}{W_a} 100\% \qquad \text{(VIII.3)}$$

The theoretical consumption of energy (kW h per 1 kg of the product) is given by

$$w_{th} = \frac{v_{th} I \tau}{G_{max}} \qquad \text{(VIII.4)}$$

where v_{th} is the theoretical voltage in the electrolyzer which is the difference between the equilibrium potentials of the anodic φ_a and cathodic φ_c reaction (in volts):

$$v_{th} = \varphi_a - \varphi_c \qquad \text{(VIII.5)}$$

The equilibrium electrode potentials are given by the Nernst equations:

$$\varphi_c = \varphi^\circ + \frac{RT}{nF} \ln a_1 \qquad \text{(VIII.6)}$$

$$\varphi_a = \varphi^\circ - \frac{RT}{nF} \ln a_2 \qquad \text{(VIII.7)}$$

where φ° is the standard electrode potential, R is the gas constant, T is the absolute temperature, a_1 and a_2 are the activities of the ions in the electrolyte solutions, n is the ion charge, and F is the Faraday constant.

The standard electrode potentials for 25 °C and the pressure 10^5 Pa are given in Table 44 for the aqueous solution activities of 1 g-equiv/litre.

The actual voltage v_a of the electrolyzer is higher than the theoretical voltage owing to polarization and overvoltage, as well as to the losses due to the ohmic resistances of the electrolyte and current leads. The actual voltage can be written as

$$v_a = (\varphi_a - \varphi_c) + \Delta\varphi_a + \Delta\varphi_c + \Sigma\, IR \qquad \text{(VIII.8)}$$

where $\Delta\varphi_a$ is the voltage compensating for the electrochemical polarization of the anode, $\Delta\varphi_c$ is the voltage compensating for the electrochemical polarization of the cathode, and $\Sigma\, IR$ is the voltage drop in the leads owing to their ohmic resistances.

The actual consumption of energy is

$$W_a = v_a I \tau / G_a \qquad \text{(VIII.9)}$$

Substitution of Eqs. (VIII.4) and (VIII.9) in Eq. (VIII.3) yields

$$\mu = \frac{v_{th}}{v_a} \eta \qquad \text{(VIII.10)}$$

Under industrial conditions the yield by current is typically 0.8-0.9 or even less for electrolysis of molten materials. The coefficient of energy utilization typically exceeds 0.5 for electrolysis of solutions and is below 0.5 for electrolysis of melts.

TABLE 44

The Standard Electrode Potentials Under Standard Conditions

Reaction	φ°, V
$Li^+ + e^- \rightleftarrows Li$	−3.05
$Cs^+ + e^- \rightleftarrows Cs$	−2.92
$Rb^+ + e^- \rightleftarrows Rb$	−2.92
$K^+ + e^- \rightleftarrows K$	−2.92
$^1/_2\, Ba^{2+} + e^- \rightleftarrows {}^1/_2\, Ba$	−2.9
$^1/_2\, Sr^{2+} + e^- \rightleftarrows {}^1/_2\, Sr$	−2.89
$^1/_2\, Ca^{2+} + e^- \rightleftarrows {}^1/_2\, Ca$	−2.87
$Na^+ + e^- \rightleftarrows Na$	−2.712
$^1/_3\, Al(OH)_4^- + e^- \rightleftarrows {}^1/_3\, Al + {}^1/_3\, OH^-$	−2.35
$^1/_2\, Mg^{2+} + e^- \rightleftarrows {}^1/_2\, Mg$	−2.34
$^1/_2\, Be^{2+} + e^- \rightleftarrows {}^1/_2\, Be$	−1.85
$^1/_2\, Al^{3+} + e^- \rightleftarrows {}^1/_3\, Al$	−1.67
$^1/_2\, (Zn)OH_4^{2-} + e^- \rightleftarrows {}^1/_2\, Zn + 2OH^-$	−1.216
$^1/_2\, Mn^{2+} + e^- \rightleftarrows {}^1/_2\, Mn$	−1.18
$^1/_2\, Zn(NH_3)_4^{2+} + e^- \rightleftarrows {}^1/_2\, Zn + 2NH_3$	−1.03
$Co(CN)_6^{3-} + e^- \rightleftarrows Co(CN)_6^{4-}$	−0.83
$^1/_2\, Zn^{2+} + e^- \rightleftarrows {}^1/_2\, Zn$	−0.762
$^1/_3\, Cr^{3+} + e^- \rightleftarrows {}^1/_3\, Cr$	−0.74
$CO_2 + H^+ + e^- \rightleftarrows {}^1/_2\, H_2C_2O_4$	−0.49
$^1/_2\, Fe^{2+} + e^- \rightleftarrows {}^1/_2\, Fe$	−0.44
$^1/_2\, Cd^{2+} + e^- \rightleftarrows {}^1/_2\, Cd$	−0.402
$^1/_2\, Co^{2+} + e^- \rightleftarrows {}^1/_2\, Co$	−0.277
$^1/_2\, Ni^{2+} + e^- \rightleftarrows {}^1/_2\, Ni$	−0.250
$^1/_2\, Sn^{2+} + e^- \rightleftarrows {}^1/_2\, Sn$	−0.136
$^1/_2\, Pb^{2+} + e^- \rightleftarrows {}^1/_2\, Pb$	−0.126
$H^+ + e^- \rightleftarrows {}^1/_2\, H_2$	0.000
$^1/_2\, S + H^+ + e^- \rightleftarrows {}^1/_2\, H_2S$	+0.141
$^1/_2\, SO_4^{2-} + 2H^+ + e^- \rightleftarrows {}^1/_2\, H_2O + {}^1/_2\, H_2SO_3$	+0.17
$^1/_2\, Cu^{2+} + e^- \rightleftarrows {}^1/_2\, Cu$	+0.345
$^1/_2\, O_2 + H_2O + 2e^- \rightleftarrows 2OH^-$	+0.40
$^1/_2\, I_2\,(kp.) + e^- \rightleftarrows I^-$	+0.53
$^1/_2\, O_2 + H^+ + e^- \rightleftarrows {}^1/_2\, H_2O_2$	+0.682
$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	+0.771
$^1/_2\, Hg^{2+} + e^- \rightleftarrows Hg$	+0.799
$Ag^+ + e^- \rightleftarrows Ag$	+0.800
$NO_3^- + 2H^+ + e^- \rightleftarrows H_2O + NO_2$	+0.81
$^1/_2\, Hg^{2+} + e^- \rightleftarrows {}^1/_2\, Hg$	+0.854
$^1/_2\, MnO_2 + 2H^+ + e^- \rightleftarrows H_2O + {}^1/_2\, Mn^{2+}$	+1.23
$^1/_2\, Cl_2 + e^- \rightleftarrows Cl^-$	+1.358

TABLE 44 (cont.)

Reaction	φ°, V
$^1/_3\,Au^{3+} + e^- \rightleftarrows {}^1/_3\,Au$	+1.5
$^1/_2\,H_2O_2 + H^+ + e^- \rightleftarrows H_2O$	+1.77
$Co^{3+} + e^- \rightleftarrows Co^{2+}$	+1.84
$^1/_2\,F_2 + e^- \rightleftarrows F^-$	+2.65

Calculations of Electrochemical Processes

Problem 1. Electrolysis of sodium chloride solution for 24 hours with the current of 15 500 A produced 4200 litres of cell liquor containing 125 g/litre of NaOH. Calculate the yield by current.

Solution. The yield can be found from Eq. (VIII.1). The actual amount of NaOH is 125 × 4200/1000 = 525 kg. The theoretical amount is given by Eq. (VIII.2): G_{max} = 555 kg. We obtain η = = 94.6%.

Problem 2. Calculate the degree of utilization of electric energy in electrolysis of sodium chloride solution if the NaCl concentration is 310 g/litre, the overvoltage for chlorine liberation is 0.192 V, the overvoltage for hydrogen liberation is 0.210 V, and the total voltage drop owing to the ohmic resistance, including that of membrane, is 1.051 V. The yield by current is 0.96.

Solution. Electrolysis of a solution of sodium chloride gives rise to chlorine and oxygen liberated at the anode (graphite) according to the following reaction equations:

$$Cl^- - e^- \longrightarrow 1/2\ Cl_2$$

and

$$2OH^- - 2e^- \rightleftarrows 1/2\ O_2 + H_2O$$

Let us determine the equilibrium potentials for the anodic reactions.

Table 44 yields the standard potentials $\varphi^\circ_{OH} = +0.40$ V and $\varphi^\circ_{Cl_2} = +1.358$ V. The equilibrium potential can then be found from the Nernst equation (VIII.7).

The concentration of the OH^- ions in the neutral saturated solution of sodium chloride is about 10^{-7} mole/litre. The activity coefficient is 0.8. We obtain

$$\varphi_{a,\,OH^-} = \varphi^\circ_{OH^-} - \frac{RT}{nF} \ln a_2 = 0.82\ V$$

The concentration of the chloride ions in the saturated solution of sodium chloride (310 g/litre) is 5.3 mole/litre and the activity coef-

ficient is 0.67. We obtain

$$\varphi_{a,\ Cl_2} = \varphi^{\circ}_{Cl^-} - \frac{RT}{nF} \ln a_2 = 1.32 \text{ V}$$

It can be seen that the discharge potential for the OH^- ions is lower than that for the Cl^- ions. However, the high overvoltage for oxygen liberation at the graphite electrode where there is practically no overvoltage for chlorine liberation makes the potential for OH^- liberation more positive than that for Cl^-. Therefore, electrolysis of saturated solutions of sodium chloride results in liberation of only chlorine at the graphite electrode.

At the cathode hydrogen is liberated according to the equation

$$2H_2O + 2e^- = H_2 + 2OH^-$$

The concentration of hydrogen ions can be found from the equation for water dissociation:

$$H_2O \rightleftarrows H^+ + OH^-$$

For this reaction we have

$$K = \frac{[H^+][OH^-]}{[H_2O]} \text{ or } K' = [H^+][OH^-]$$

At 25 °C $K' = 1.05 \times 10^{-14}$ so that $[H^+] = 1.05 \times 10^{-14}/[OH^-]$. The concentration of the OH^- ions in the cathodic space is equal to the molar concentration of sodium hydroxide which is completely ionized.

However, to calculate the equilibrium potential from the Nernst equation we have to know not the concentration of the ions OH^- but their activity

$$a_1 = C_{OH^-} f_{OH^-} \qquad \text{(VIII.11)}$$

Since the electrolyte contains sodium chloride apart from sodium hydroxide the former affects the value of the activity coefficient f_{OH^-}. This effect can be estimated only from the experimental data. To make such an estimate we should know the ionic strength of the catholyte and use the following rule: the activity coefficient of a given ion is the same in all solutions with the same ionic strength.

The ionic strength of a solution is given by

$$I = 1/2 (m_1 n_1^2 + m_2 n_2^2 + \ldots) \qquad \text{(VIII.12)}$$

where m is the molar concentration of each ion and n is the ion charge.

For the solution containing 100 g/litre of NaOH and 190 g/litre of NaCl we obtain $m_{Na^+} = 100/40 + 190/58.5 = 5.75$, $m_{Cl^-} = 190/58.5 = 3.25$, and $m_{OH^-} = 100/40 = 2.5$. Hence, we obtain $I = 5.75$.

The activity coefficient for the NaOH solution with the ionic strength 5.75 is 0.73. Hence, the activity of the ions H^+ in the electrolyte is

$$a_1 = C_{H^+} f_{H^+} = 1.05 \times 10^{-14} \times 0.73/2.5 = 0.307 \times 10^{-14}$$

and the equilibrium potential is

$$\varphi_{H_2} = 0.0 + \frac{RT}{nF} \ln a_1 = -0.53 \text{ V}$$

The theoretical voltage of dissociation of sodium chloride is

$$v_{th} = \varphi_a - \varphi_c = 1.32 - (-0.53) = 1.85 \text{ V}$$

The actual voltage of dissociation is $v_a = 1.32 - (-0.53) + (0.192 + 0.21) + 1.051 = 3.3$ V.

If the yield by current is 0.96 we obtain $\mu = 54\%$.

Problem 3. A 10×10 cm metal plate is plated with 50 μm nickel in electrolyte solution containing the Ni^{2+} ions. Calculate the time needed to produce the specified thickness of plating for the current of 2.5 A. The conditions of electrolysis provide for uniform plating. The yield by current is 94.4%.

Solution. The volume of the nickel layer is $10 \times 10 \times 2 \times 0.005 = 1.0 \text{ cm}^3$. Since the nickel density is 8900 kg/m³ the amount of deposited nickel is $G_a = 8.9$ g. The electric charge needed for electrolysis is $8.9 \times 2 \times 26.8/58.69 = 8.12$ A h (here 58.69 is the atomic mass of nickel). As the yield by current is 0.944 the actual electric charge is 8.12/0.944 = 8.6 A h. Hence, we have $I\tau = 8.6$ A h and $\tau = 8.6/2.5 = 3.44$ h.

Problem 4. Calculate the additional electric energy consumption due to the overvoltage of 0.25 V in electrolytic production of hydrogen per 1 ton of hydrogen.

Solution. The consumption of electric energy in electrolytic production of hydrogen is 26.8 A h per 1 equivalent. The additional energy consumption due to the overvoltage is $26.8 \times 0.25 = 6.7$ W h or 6.7×10^6 W h = 6700 kW h per 1 ton of hydrogen.

Problem 5. Calculate the yield by current and the energy cnosumption in electrolysis of KCl solution. The cathode compartment of the laboratory electrolyzer contains 500 ml of the solution. The copper cathode of the in-series Coulomb meter increased its mass by 5 g. In assaying the KOH concentration in the electrolyte in the cathode compartment 25 ml of the 0.1 *N* HCl solution were consumed for 10 ml of the electrolyte. The voltage in the electrolyzer was 4.5 V.

Solution. The electric charge consumed in electrolysis can be found from the increase in mass of the copper cathode from Eq. (VIII.2): $I\tau = 26.8 \times 5/32 = 4.2$ A h. The theoretical amount of KOH produced by electrolysis is $G_{max} = 4.2 \times 56/26.8 = 8.8$ g. The actual amount of KOH is $G_a = 25 \times 0.0056 \times 500/10 = 7$ g.

The yield by current is $\eta = 7/8.8 = 0.795$. The consumption of energy per 1 kg of KOH is $4.5 \times 4.2 \times 1000/7 = 2700$ W h.

Problem 6 (see [2], p. 258). Calculate the time of electrolysis needed to produce 0.6 litre of oxyhydrogen gas at the temperature 20 °C and the pressure 0.97×10^5 Pa if the current is 2 A.

Solution. The oxyhydrogen gas contains 2 parts by volume of hydrogen and 1 part of oxygen. Hence, 0.6 litre of the gas contains 0.4 litre of hydrogen and 0.2 litre of oxygen. Using the Mendeleev-Clapeyron equation find the masses of hydrogen and oxygen:

$$G_{H_2} = 2 \times 0.97 \times 10^5 \times 0.4/10^5 \times 0.0821 \times 293 = 0.0325 \text{ g}$$

$$G_{O_2} = 32 \times 0.97 \times 10^5 \times 0.2/10^5 \times 0.0821 \times 293 = 0.2591 \text{ g}$$

The time needed to produce 0.6 litre of the oxyhydrogen gas is

$$\tau = 26.8\ G/IE = 26.8 \times 0.0325/1 \times 2 = 0.433 \text{ h}$$

or

$$\tau = 26.8 \times 0.2591/8 \times 2 = 0.433 \text{ h}$$

(here 1 is the atomic mass of hydrogen and 8 is the atomic mass of oxygen).

Problem 7 ([33], p. 573). Calculate the amount of heat evolved with electrochemical production of zinc. The electrolysis current is 10 000 A, the voltage is 3.4 V. The yield by current for zinc is 80%. The concentration of H_2SO_4 in the discharged electrolyte is 80 g/litre, the zinc concentration in the fresh electrolyte is 118 g/litre. The process is described by the following overall equation:

$$ZnSO_4 + 51H_2O \longrightarrow Zn + 0.5O_2 + H_2SO_4 \cdot 50H_2O$$

(the concentration of H_2SO_4 in the discharged solution approximately corresponds to $50H_2O$). The heat of dilution of $ZnSO_4$ is ignored. The main process is accompanied by the secondary reaction

$$H_2O = H_2 + 0.5O_2, \quad q_1 = 287.5 \text{ kJ}$$

Solution. Calculation of the heat of the main process:

$$ZnSO_4 + H_2O \longrightarrow ZnO + H_2SO_4 \qquad q_2 = 84 \text{ kJ}$$

$$ZnO \longrightarrow Zn + 0.5O_2 \qquad q_3 = 354 \text{ kJ}$$

$$H_2SO_4 + 50H_2O \longrightarrow H_2SO_4 \cdot 50H_2O \qquad q_4 = -71 \text{ kJ}$$

$$ZnSO_4 + 51H_2O \longrightarrow Zn + 0.5O_2 + H_2SO_4 \cdot 50H_2O \qquad q = 366 \text{ kJ}$$

Since the passage of the electric charge of 1 A h results in liberation of 1.219 g of zinc the total amount of zinc liberated per 1 hour in the process is $10\,000 \times 0.8 \times 1.219 = 9760$ g.

The amount of water dissociated with passage of 1 A h is 0.336 g so that the total amount of water dissociated in 1 hour is $10\,000 \times \times 0.2 \times 0.336 = 672$ g.

The amount of heat consumed with zinc liberation is 366 × × 9760/65.4 = 54 500 kJ. The amount of heat consumed with dissociation of water is 672 × 287.5/18 = 10 720 kJ. The total amount of heat is 54 500 + 10 720 = 65 220 kJ.

The heat supplied to the electrolyzer per 1 hour by the current is $Q = 3.62 \times 10\,000 \times 3.4 = 123\,000$ kJ. The heat consumed for heating the electrolyzer is $Q_1 = 123\,000 - 65\,220 = 57\,780$ kJ.

If the electrolyzer is cooled to 40 °C with the cooling water (the starting temperature 15 °C, the final temperature 35 °C) and we ignore the heat losses by radiation, convection and evaporation the amount of the cooling water is approximately 13 700/(35 — 15) × 1000 = = 0.689 m³/h per 1 electrolyzer.

The discharged solution contains 80 g/litre of H_2SO_4. According to the reaction equation

$$\underset{}{ZnSO_4 + H_2O} = \underset{65}{Zn} + 0.5O_2 + \underset{98}{H_2SO_4}$$

we find that the mass of zinc evolved per 1 litre of the electrolyte is 80 × 65/98 = 53 g.

The amount of electrolyte fed into the electrolyzer is 9760/53 = = 184 litres. If the temperature of the fresh solution is 20 °C the heat consumed for its heating up to 40 °C is 184 (40 — 20) × 4.18 = = 15 400 kJ (the specific heat of the solution is assumed to be 4.18 kJ/kg K). This consumption of heat makes it possible to reduce the flow rate of the cooling water.

Problem 8 (see [33], p. 279). Calculate the number of electrolyzers for producing 50 000 tons of aluminium per year. Find the mean voltage for the electrolyzer and draw up the voltage balance. The electrolyzers with self-baking anodes consume the current of 50 000 A. The yield by current is 89%. The yield of aluminium is 62 g per 1 kW h. The aluminium loss with remelting is 2%. The time losses for maintenance are 3%.

Solution. The electrolyzer is in operation for 365 × 24 — 365 × × 24 × 0.03 = 8500 hours a year.

Taking into account the losses for remelting the productivity of the plant should be (50 000 + 50 000 × 0.02)/8500 = 6000 kg of aluminium per 1 hour.

The amount of aluminium produced per 1 A h is 0.335 × 0.89 = = 0.3 g (here 0.335 is the electrochemical equivalent for aluminium).

The 50 000 A electrolyzer produces 50 000 × 0.3/1000 = 15 kg of aluminium per 1 hour. The required number of electrolyzers is 6000/15 = 400.

The mean electrolyzer voltage is 1000 × 0.335 × 0.89/62 = 4.8 V. The electrodic processes occurring with electrolysis of the cryolite-alumina melt are too complicated to be analysed here since we do not know the ionic potentials and even the nature and concentra-

tions of the ions. Therefore, we shall assume on the basis of experimental results that the electrolyzer voltage is 1.7 V.

The anodic effect is a temporary increase of voltage owing to formation of the gaseous insulating layer around the anode. The anodic effect is eliminated by mixing of the electrolyte.

The frequency of the anodic effect is assumed to be one episode of 6 min every two days.

The voltage increase by the anodic effect is 30 V. The mean voltage increase due to the anodic effect is $6 \times 30/2 \times 24 \times 60 = 0.06$ V.

Apart from decomposition voltage and the voltage increase due to the anodic effect, the voltage drop occurs in the electrolyte and at the contacts: $4.8 - 1.7 - 0.06 = 3.04$ V.

The external ("non-heating") contacts and leads account for 12% of the voltage drop: $3.04 \times 0.12 = 0.36$ V. The voltage drop on the internal heating contacts and leads amounts to 20%, that is, $3.04 \times \times 0.2 = 0.61$ V.

Electrolyte accounts for the rest of the voltage drop: $3.04 - 0.36 - - 0.61 = 2.07$ V.

The voltage balance is summarized below:

Decomposition voltage	1.7 V
Voltage drop in electrolyte	2.07 V
External contacts and leads	0.36 V
Internal contacts and leads	0.61 V
Mean voltage increase by anodic effect	0.06 V
Total:	4.8 V

Further Problems for Students

1. A metallic article has to be plated with 0.2 mm nickel. The surface area of the article is 250 cm^2. Calculate the duration of electrolysis with the 2.8 A current if the yield by current is 91%.
2. Calculate the decomposition potential of NaOH in electrolysis of molten NaOH at 300 °C.
3. Calculate the amount of hydrogen evolved with electrolysis of dilute H_2SO_4 solution after passage of the charge of 7.5 A h.
4. Calculate the energy needed for production of 1 kg of aluminium in a 4.8 V electrolyzer with the yield by current of 89%.
5. Calculate the coefficient of utilization of energy in production of metallic sodium from molten NaOH in a 4.5 V electrolyzer with the yield by current of 45%.
6. The consumption of energy in a 2 V electrolyzer for production of 1 kg of copper is 2.25 kW h. Calculate the yield by current.

Appendix I

Molecular and Atomic Volumes of Some Substances

Substance	cm^3/mole	Substance	cm^3/mole
H_2	14.3	I	37
O_2	25.6	H	3.7
N_2	31.2	C	14.8
Air	29.9	N (in primary amines)	10.5
CO	30.7	N (in secondary amines)	12
CO_2	34	N (in other compounds)	15.6
SO_2	44.8	O (in methyl ester and ether)	9.1
N_2O	36.4	O (in diethyl ester and ether)	9.9
NO	23.6	O (in higher esters and ethers)	11.0
NH_3	25.8	O (in acids)	12.0
H_2O	18.9	O (bound to S, P, and N)	8.3
H_2S	32.9	O (in other compounds)	7.4
COS	51.5	S	25.6
Cl_2	48.4	Three-member ring (deduct)	6.0
Br_2	53.2	Four-member ring (deduct)	8.5
I_2	71.5	Five-member ring (deduct)	11.5
Br	27	Six-member ring (deduct)	15.0
Cl	24.6	Naphthalene ring (deduct)	30.0
F	8.7	Anthracene ring (deduct)	47.5

Appendix II

Diffusion Coefficients of Some Gases (D_g—in gases at 0 °C and 10^5 Pa, D_l in water at 20 °C; in cm^2/s)

Gas	D_g in air	D_g in CO_2	D_g in H_2	$D_l \times 10^5$
Nitrogen	0.132	0.146	0.674	1.64
Nitric oxide	0.145	—	—	1.54
Nitrogen dioxide	0.119	—	—	—

Appendix II (cont.)

Gas	D_g in air	D_g in CO_2	D_g in H_2	$D_l \times 10^5$
Ammonia	0.198	—	0.745	1.76
Acetone	0.082	—	—	1.03
Benzene	0.077	0.053	0.295	—
Water (steam)	0.220	0.139	0.752	—
Hydrogen	0.611	0.550	—	5.13
Diethyl ether	0.078	0.055	0.296	—
Oxygen	0.178	—	0.697	1.8
Methane	0.223	0.153	0.625	2.06
Methanol	0.132	0.088	0.506	1.28
Hydrogen sulphide	0.127	—	—	1.41
Carbon sulphide	0.089	0.063	0.369	—
Sulphur dioxide	0.122	—	0.480	1.47
Sulphur trioxide	0.094	—	—	—
Toluene	0.071	—	—	—
Carbon dioxide	0.138	—	0.550	1.77
Carbon monoxide	0.202	0.137	0.051	1.19
Acetic acid	0.106	0.072	0.416	0.88
Chlorine	0.124	—	—	1.22
Hydrogen chloride	0.130	—	0.712	2.64
Ethanol	0.102	0.068	0.375	1.0
Ethyl acetate	0.072	0.049	0.273	—
Ethylene	0.152	—	0.486	1.59

Appendix III

Packing Ring and Lump Parameters

Packing type	Size, mm	No. of elements in 1 cm^3	Free volume, m^3/m^3	Specific surface area, m^2/m^3	Density, kg/m^3
Rings:					
Porcelain	8 × 8 × 1.5	1 465 000	0.64	570	600
Ceramic	15 × 15 × 2	250 000	0.70	330	690
Ceramic	25 × 25 × 3	53 200	0.74	204	532
Ceramic	35 × 35 × 4	20 200	0.78	140	505
Ceramic	50 × 50 × 5	6 000	0.785	87.5	530
Iron	35 × 35 × 2.5	19 000	0.83	147	—
Iron	50 × 50 × 1	6 000	0.95	110	430

Appendix III (cont.)

Packing type	Size, mm	No. of elements in 1 cm^3	Free volume, m^3/m^3	Specific surface area, m^2/m^3	Density, kg/m^3
Gravel	42	14 400	0.388	80.5	—
Andesite (lumps)	43.2	12 600	0.565	68	1 200
Coke (lumps)	42.6	14 000	0.56	77	455
Coke (lumps)	40.8	15 250	0.545	86	585
Coke (lumps)	28.6	27 700	0.535	110	660
Coke (lumps)	24.4	64 800	0.532	120	600
Catalyst for ammonia synthesis (lumps)	6.1	5 200 000	0.465	960	2 420
Catalyst for CO conversion (pellets)	$d=11.5$, $h=6$	1 085 000	0.38	460	1 100
Vanadium catalyst (pellets)	$d=11$, $h=6.5$	1 000 000	0.43	415	614

Appendix IV

Gas Densities

Gas	Density, kg/m^3	Gas	Density, kg/m^3
Nitrogen	1.25055	Dry air	1.2929
Atmospheric nitrogen (N_2+Ar)	1.2568	Oxygen	1.42895
Nitrogen dioxide	2.0539	Methane	0.7168
Nitric oxide	1.3402	Sulphur dioxide	2.9268
Ammonia	0.7710	Sulphur trioxide	3.574
Argon	1.7837	Hydrogen sulphide	1.539
Hydrogen	0.08988	Carbon dioxide	1.9769
Hydrogen chloride	1.6391	Carbon monoxide	1.2504
Water vapour	0.8043	Chlorine	3.214
		Ethane	1.356

Appendix V

Equilibrium Constants of the Fundamental Reactions at the Pressure of 1.01325×10^5 Pa (1 atm)

Reaction	Equilibrium constants: Formula	Equilibrium constants: Value
$2H \rightleftarrows H_2$	$K_p = \frac{p_{H_2}}{p_H^2}$	$\log K_p = \frac{22\,370}{T} - 1.504 \log T - 0.767$
$2Cl \rightleftarrows Cl_2$	$K_p = \frac{p_{Cl_2}}{p_{Cl}^2}$	$\log K_p = \frac{12\,600}{T} - 0.535 \log T - 4.090$
$2Br\,(g) \rightleftarrows Br_2\,(g)$	$K_p = \frac{p_{Br_2}}{p_{Br}^2}$	$\log K_p = \frac{10\,000}{T} - 0.763 \log T + 1.035 \times 10^{-4} T - 3.341$
$2I\,(g) \rightleftarrows I_2\,(g)$	$K_p = \frac{p_{I_2}}{p_I^2}$	$\log K_p = \frac{7550}{T} - 1.75 \log T + 4.09 \times 10^{-4} T + 0.44$
$Cl_2 + H_2 \rightleftarrows 2HCl$	$K = \frac{[HCl]^2}{[Cl_2]\,[H_2]}$	$\log K = \frac{9586}{T} - 0.440 \log T + 2.16$
$Br_2 + H_2 \rightleftarrows 2HBr$	$K = \frac{[HBr]^2}{[Br_2]\,[H_2]}$	$\log K = \frac{5223}{T} - 0.553 \log T + 2.72$
$I_2\,(g) + H_2 \rightleftarrows 2HI$	$K = \frac{[HI]^2}{[I_2]\,[H_2]}$	$\log K = \frac{540.4}{T} - 0.503 \log T + 2.35$
$2Cl_2 + 2H_2O \rightleftarrows 4HCl + O_2$	$K_p = \frac{p_{HCl}^4 p_{O_2}}{p_{Cl_2}^2 p_{H_2O}^2}$	$\log K_p = \frac{-5150}{T} + 2.136 \log T + 8.57 \times 10^{-4} T - 6.83 \times 10^{-8} T^2 - 0.296$
$CO + Cl_2 \rightleftarrows COCl_2$	$K_p = \frac{p_{COCl_2}}{p_{CO} p_{Cl_2}}$	$\log K_p = \frac{5020}{T} - 1.75 \log T - 1.158$
$2H_2 + O_2 \rightleftarrows 2H_2O$	$K_C = \frac{[H_2O]^2}{[H_2]^2\,[O_2]}$	$\log K_C = \frac{24\,900}{T} - 1.335 \log T + 9.65 \times 10^{-5} T - 1.37 \times 10^{-7} T^2 + 6.65 \times 10^{-11} T^3 - 1.907 \times 10^{-18} T^5 + 1.08$

Appendix V (cont.)

Equilibrium constants		
Reaction	Formula	Value
$2CO+O_2 \rightleftarrows 2CO_2$	$K_C=\frac{[CO_2]^2}{[CO]^2[O_2]}$	$\log K_C=\frac{29\,500}{T}-1.75\log T+$ $+1.215\times10^{-3}T-1.35\times$ $\times10^{-7}T^2-3.29$
$CO+H_2O \rightleftarrows H_2+CO_2$	$K=\frac{[H_2][CO_2]}{[CO][H_2O]}$	$\log K=\frac{2203.24}{T}+5.1588\times$ $\times10^{-5}T+2.5426\times10^{-7}T^2-$ $-7.4617\times10^{-11}T^3-2.3$
$S_2\,(g)+2H_2 \rightleftarrows 2H_2S$	$K_p=\frac{p^2_{H_2S}}{p_{S_2}p^2_{H_2}}$	$\log K_p=\frac{8400}{T}-0.974\log T-$ $-7.2\times10^{-4}T-0.72$
$2SO_2+O_2 \rightleftarrows 2SO_3$	$K_C=\frac{[SO_3]^2}{[SO_2]^2[O_2]}$	$\log K_C=\frac{10\,373}{T}+$ $+2.222\log T-14.585$
	$K_p=\frac{p^2_{SO_2}p_{O_2}}{p^2_{SO_3}}$	$\log K_p=-\frac{9480}{T}+$ $+6.38\log T-0.0049T-5.41$
$SO_3+H_2O\,(g) \rightleftarrows H_2SO_4\,(g)$	$K_C=\frac{[H_2SO_4]}{[H_2O][SO_3]}$	$\log K_C=\frac{5000}{T}-0.75\log T+$ $+5.7\times10^{-4}T-4.086$
$2NO+O_2 \rightleftarrows 2NO_2$	$K_p=\frac{p^2_{NO_2}}{p^2_{NO}p_{O_2}}$	$\log K_p=\frac{5749}{T}-1.70\log T+$ $+5\times10^{-4}T-2.839$
$2NO_2 \rightleftarrows N_2O_4$	$K_p=\frac{p_{N_2O_4}}{p^2_{NO_2}}$	$\log K_p=\frac{2692}{T}-1.75\log T-$ $-4.83\times10^{-3}T+7.144\times$ $\times10^{-6}T^2-3.062$
$N_2+O_2 \rightleftarrows 2NO$	$K_C=\frac{[NO]^2}{[N_2][O_2]}$	$\log K_C=-\frac{9460}{T}+1.09$
$1/2N_2+3/2H_2 \rightleftarrows NH_3$	$K_p=\frac{p_{NH_3}}{p^{3/2}_{H_2}p^{1/2}_{N_2}}$	$\log K_p=\frac{2098.2}{T}-2.509\log T-$ $-1.006\times10^{-4}T+16\,859\times$ $\times10^{-7}T^2+2.10$
$C+2H_2 \rightleftarrows CH_4$	$K_p=\frac{p_{CH_4}}{p^2_{H_2}}$	$\log K_p=\frac{3348}{T}-5.957\log T+$ $+1.86\times10^{-3}T-0.1095\times$ $\times10^{-6}T^2+11.79$

Appendix V (cont.)

Equilibrium constants		
Reaction	Formula	Value
$CO+2H_2 \rightleftarrows CH_3OH$	$K_p=\frac{p_{CH_3OH}}{p_{CO}p_{H_2}^2}$	$\log K_p=\frac{3724}{T}-9.1293\log T+$ $+3.08\times10^{-3}T+13.412$
$C+O_2=CO_2$	$K_p=\frac{p_{O_2}}{p_{CO_2}}$	$\log K_p=\frac{-20582.8}{T}+$ $+0.302\log T-1.43\times10^{-4}T+$ $+0.196\times10^{-7}T^2-0.62$
$2C+O_2 \rightleftarrows 2CO$	$K_p=\frac{p_{O_2}}{p_{CO}^2}$	$\log K_p=\frac{-11635.1}{T}-$ $-2.1656\log T+0.9394\times$ $\times10^{-3}T-0.1064\times10^{-6}T^2-$ -3.394
$2C+2H_2 \rightleftarrows C_2H_4$	$K_p=\frac{p_{C_2H_4}}{p_{H_2}^2}$	$\log K_p=-\frac{3540}{T}-$ $-5.589\log T+1.025\times10^{-3}T+$ $+0.175\times10^{-6}T^2+13.04$
$2C+H_2 \rightleftarrows C_2H_2$	$K_p=\frac{p_{C_2H_2}}{p_{H_2}}$	$\log K_p=-\frac{1190}{T}+$ $+2.37$ (approx.)
$C+2H_2O \rightleftarrows CO_2+2H_2$	$K_p=\frac{p_{CO_2}p_{H_2}^2}{p_{H_2O}^2}$	$\log K_p=-\frac{4533.3}{T}+$ $+0.6446\log T+0.8646\times$ $\times10^{-3}T+0.1814\times10^{-6}T^2+$ $+2.336$
$C+S_2 \rightleftarrows CS_2$ (g)	$K_C=\frac{[S_2]}{[CS_2]}$	$\log K_C=-\frac{1890}{T}+$ $+1.75\log T-1.56$ (approx.)
$CO+H_2 \rightleftarrows HCOH$	$K_p=\frac{p_{CO}p_{H_2}}{p_{HCOH}}$	$\log K_p=-\frac{374}{T}+$ $+5.431$ (approx.)
$CH_4+H_2O \rightleftarrows CO+3H_2$	$K_p=\frac{p_{CO}p_{H_2}^3}{p_{CH_4}p_{H_2O}}$	$\log K_p=-\frac{9874}{T}+$ $+7.14\log T-1.88\times10^{-3}T+$ $+0.094\times10^{-6}T^2-8.64$

Appendix V (cont.)

Equilibrium constants		
Reaction	Formula	Value
$CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$	$K_p = \frac{p_{CO_2} p_{H_2}^4}{p_{CH_4} p_{H_2O}^2}$	$\log K_p = -\frac{7674}{T} + 6.23 \log T - 0.906 \times 10^{-3} T - 0.0546 \times 10^{-6} T^2 - 8.72$
$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$	$K_p = \frac{p_{CO}^2 p_{H_2}^2}{p_{CH_4} p_{CO_2}}$	$\log K_p = -\frac{11087.7}{T} + 3.1127 \log T - 2.8524 \times 10^{-3} T + 13.216 \times 10^{-6} T^2 - 8.528$
$C_2H_4 + H_2O \rightleftarrows C_2H_5OH$	$K_p = \frac{p_{C_2H_4} p_{H_2O}}{p_{C_2H_5OH}}$	$\log K_p = -\frac{1090}{T} + 4.71 \log T - 2.35 \times 10^{-3} T - 7.05$
$C_6H_6 + 3H_2 \rightleftarrows C_6H_{12}$	$K_p = \frac{p_{C_6H_6} p_{H_2}^3}{p_{C_6H_{12}}}$	$\log K_p = -\frac{9530}{T} + 9.9194 \log T - 2.285 \times 10^{-3} T - 8.565$
$C_2H_5OH \rightleftarrows CH_3COH + H_2$	$K_p = \frac{p_{CH_3COH} p_{H_2}}{p_{C_2H_5OH}}$	$\log K_p = -\frac{2492}{T} + 2.0132 \log T - 2.186$
$2S \rightleftarrows S_2$	$K_C = \frac{[S]^2}{[S_2]}$	$\log K_C = -\frac{26\,250}{T} + 8.58$
$3S_2 \rightleftarrows S_6$	$K_p = \frac{p_{S_2}^3}{p_{S_6}}$	$\log K_p = -\frac{14\,000}{T} + 3.5 \log T + 5.325$
$2SO_2 + 4H_2 \rightleftarrows S_2 + 4H_2O$	$K_p = \frac{p_{SO_2}^2 p_{H_2}^4}{p_{S_2} p_{H_2O}^4}$	$\log K_p = -\frac{13\,810}{T} - 0.877 \log T + 2.67 \times 10^{-3} T - 0.46 \times 10^{-6} T^2 + 3.38$
$2SO_2 + 4CO \rightleftarrows S_2 + 4CO_2$	$K_p = \frac{p_{SO_2}^2 p_{CO}^4}{p_{CO_2}^4 p_{S_2}}$	$\log K_p = -\frac{23\,000}{T} + 4.34 \log T - 1.62 \times 10^{-3} T + 20.23 \times 10^{-6} T^2 - 2.43$

Appendix V (cont.)

Equilibrium constants		
Reaction	Formula	Value
$4NH_3+5O_2 \rightleftarrows 4NO+6H_2O$	$K_p=\frac{p^4_{NH_3}p^5_{O_2}}{p^4_{NO}p^6_{H_2O}}$	$\log K_p=-\frac{47\,500}{T}-1.75\log T-8.4$
$4NH_3+3O_2 \rightleftarrows 2N_2+6H_2O$	$K_p=\frac{p^4_{NH_3}p^3_{O_2}}{p^2_{N_2}p^6_{H_2O}}$	$\log K_p=-\frac{66\,250}{T}-1.75\log T-5.2$
$2Me+O_2 \rightleftarrows 2MeO+q$ Me is the bivalent atom (Ca, Mg, etc.); q is the heat effect of the reaction at 20 °C	$K_p=p_{O_2}$	$\log K_p=-\frac{q}{4.573\,T}+1.75\log T+2.8$
$MeCO_3 \rightleftarrows MeO+CO_2+q$	$K_p=p_{CO_2}$	$\log K_p=-\frac{q}{4.573\,T}+1.35\log T+3.2$
$Fe_3O_4+CO \rightleftarrows 3FeO+CO_2$	$K_p=\frac{p_{CO_2}}{p_{CO}}$	$\log K_p=-\frac{1373}{T}-0.341\log T+0.41\times10^{-3}T+2.303$
$FeO+CO \rightleftarrows Fe+CO_2$	$K_p=\frac{p_{CO}}{p_{CO_2}}$	$\log K_p=-\frac{381}{T}+2.11\log T-0.395\times10^{-3}T-5.357$
$PbO+CO \rightleftarrows Pb+CO_2$	$K_p=\frac{p_{CO}}{p_{CO_2}}$	$\log K_p=-\frac{3250}{T}+0.417\times10^{-3}T+0.3$
$Cu_2O+CO \rightleftarrows 2Cu+CO_2$	$K_p=\frac{p_{CO}}{p_{CO_2}}$	$\log K_p=-\frac{5980}{T}+0.74\log T-0.306\times10^{-3}T+0.11\times10^{-6}T^2-1.53$
$ZnO+CO \rightleftarrows Zn_{(g)}+CO_2$	$K_p=\frac{p_{Zn}p_{CO_2}}{p_{CO}}$	$\log K_p=-\frac{10\,360}{T}-0.348\log T-0.72\times10^{-3}T+0.137\times10^{-6}T^2+8.36$
$MgO+C \rightleftarrows Mg_{(g)}+CO$	$K_p=p_{Mg}p_{CO}$	$\log K_p=-\frac{35\,520}{T}+10.33$ (approx.)

Appendix VI

Some Kinetic Equations Used in Modelling of Chemical Processes

Process	Catalyst	Equation
Ammonia synthesis	Iron	$u = k_1 p_{N_2} \left(\frac{p_{H_2}^3}{p_{NH_3}^2} \right)^m - k_2 \left(\frac{p_{NH_3}^2}{p_{H_2}^3} \right)^{1-m}$
	Iron, in the presence of steam	$u = \frac{k_1 p_{N_2} - k_2 p_{NH_3}^2 / p_{H_2}^3}{\left(\frac{p_{NH_3}^2}{p_{H_2}^3} + c \frac{p_{H_2O}}{p_{H_2}} \right)^m}$
Oxidation of sulphur dioxide	Vanadium	$u = k p_{O_2} \frac{p_{SO_2}}{p_{SO_2} + A p_{SO_3}} \times \left[1 - \left(\frac{p_{SO_3}}{K_p p_{SO_2} \sqrt{p_{O_2}}} \right)^2 \right]$
		$u = k_1 \frac{p_{O_2} - \frac{1}{K_p} \left(\frac{p_{SO_3}}{p_{SO_2}} \right)^2}{\left(\frac{p_{SO_3}^2}{p_{SO_2}} + B \frac{p_{SO_3}}{p_{SO_2}} \right)^{0.5}}$
		$\log B = -\frac{12\,080}{T} + 17.55$
Vinyl chloride synthesis	Mercury	$u = \frac{k p_{C_2H_2} p_{HCl}}{k' + p_{HCl}}$
Carbon monoxide conversion	Iron-chromium, oxide	$u = \frac{k p_{H_2O} p_{CO} - \frac{1}{k} p_{CO_2} p_{H_2}}{A p_{H_2O} + p_{CO_2}}$
Methane conversion	Nickel	$u = \frac{k p_{CH_4}}{1 + a \frac{p_{H_2O}}{p_{H_2}} + b p_{CO}}$
		$u = 2.1 \times 10^4 A e^{-19\,400/RT} p_{CH_4}$

Appendix VI (cont.)

Process	Catalyst	Equation
Vinyl acetate synthesis	Acetate zinc	$u=\frac{k_2 p_{C_2H_4}}{1+k_1 p_{CH_3COOH}}$
Synthesis of higher alcohols	Iron	$\frac{dc}{d\tau}=k$
Methanol synthesis	Zinc-chromium	$u=k_1 p_{H_2}\left(\frac{p_{CO}}{p_{CH_3OH}}\right)^{0.5\alpha}-$ $-k_2\left(\frac{p_{CH_3OH}}{p_{CO}}\right)^{0.5\alpha}$ $\alpha=0.5$
Methanol oxidation	Iron-molybdenum	$\frac{dx}{d\tau}=k_1(1-x)$ $\frac{dz}{d\tau}=k_2\frac{y}{1+aC_1x}$
Catalystic removal of oxygen from gases by hydration	Palladium	$-\frac{dp_{O_2}}{d\tau}=kp_{O_2}$
Isotope exchange in production of heavy water	Nickel	$\frac{d(HD)}{d\tau}=k_1 p_{HDO}\left(\frac{p_{H_2}}{p_{H_2O}}\right)^{0.5}-$ $-k_2 p_{HD}\left(\frac{p_{H_2O}}{p_{H_2}}\right)^{0.5}$
Butane dehydration	Alumina-chromium	$u=k_1\frac{p_{C_4H_{10}}}{\sqrt{p_{C_4H_8}}}\times$ $\times\left(1-\frac{p_{C_4H_8}p_{H_2}}{K_p p_{C_4H_{10}}}\right)$
Butylene dehydration (main reaction)	K-16	$u=k_1 p_{C_4H_8}^{0.35}\left(1-\frac{p_{C_4H_6}p_{H_2}}{K_p p_{C_4H_8}}\right)$

Appendix VI (concl.)

Process	Catalyst	Equation
Phosgene synthesis	—	$u = k_1 p_{CO} p_{Cl_2}^{3/2} - k_2 p_{COCl_2} p_{Cl_2}^{1/2}$
Ammonia oxidation to nitrogen oxides	Platinum	$u = k p_{NH_3}$
	$MnO - Bi_2O_3 - Al_2O_3$	$u = \frac{A p_{NH_3} p_{O_2}^{0.5}}{[1 + (B p_{O_2})^{0.5}]}$

Appendix VII

The Main Thermodynamic Parameters of Some Substances Under the Standard Conditions

(ΔH°_{298} — enthalpy of formation, ΔG°_{298} — Gibbs energy (the isobaric and isothermic potential of formation), S°_{298} — entropy, G — gas, L — liquid, Cryst — crystal; in some cases modification is noted)

Substance	State	ΔH°_{298}, kJ/mole	ΔG°_{298}, kJ/mole	S°_{298}, J/mole K
C	Diamond	+1.8966	+2.900	2.377
H_2O	L	−285.830	−237.435	70.18
D_2O	L	−294.609	−243.475	75.9
H_2O	G	−241.818	−228.605	188.723
CO	G	−110.525	−137.152	197.564
CO_2	G	−393.509	−394.363	213.65
NO	G	+90.249	+90.75	210.65
NO_2	G	+33.179	+51.29	239.95
SO_2	G	−296.855	−300.2	248.11
SO_3	G	−395.806	−331.1	256.65
SiO_2	α-quartz	−910.94	−856.67	41.84
TiO_2	Rutile	−943.49	−88.18	12.01
MgO	Cryst	−601.70	−569.44	26.94
CaO	Cryst	−535.09	−605.55	39.75

Appendix VII (cont.)

Substance	State	ΔH°_{298}, kJ/mole	ΔG°_{298}, kJ/mole	S°_{298}, J/mole K
Al_2O_3	α-corundum	—1675.7	—1582.4	50.91
HCl	G	—92.307	—95.286	186.799
H_2SO_4	L	—813.7	—689.9	156.90
NH_3	G	—48.11	—16.48	192.34
KCl	Cryst	—436.68	—408.78	82.55
KBr	Cryst	—392.17	—378.78	95.86
$MgCl_2$	Cryst	—641.62	—592.12	89.63
$Mg(OH)_2$	Cryst	—924.7	—833.9	63.2
Na_2CO_3	Cryst	—1130.37	—1048.09	138.78
K_2CO_3	Cryst	—1150.2	—1064.4	155.52
$MgCO_3$	Cryst	—1112.94	—1029.35	65.7
$MgSO_4$	Cryst	—1261.77	—1147.50	91.38
$CaO \cdot Al_2O_3$	Cryst	—2326.3	—2208.7	114.22
$3CaO \cdot Al_2O_3$	Cryst	—3587.8	—3411.6	205.9

Appendix VIII

The Main Thermodynamic Parameters of Some Organic Compounds Under the Standard Conditions (notation see in Appendix VII)

Substance	State	ΔH°_{298}, kJ/mole	ΔG°_{298}, kJ/mole	S°_{298}, J/mole K
Methane CH_4	G	—74.85	—50.84	186.27
Ethane C_2H_6	G	—85.94	—32.93	229.49
Ethylene C_2H_4	G	52.30	268.16	219.45
Acetylene C_2H_2	G	229.66	209.20	200.83
Benzene C_6H_6	L	49.03	124.35	173.26
Benzene C_6H_6	G	82.93	129.66	269.20
Methanol CH_3OH	L	—238.57	—166.23	126.76
Methanol CH_3OH	G	—201.17	—162.51	239.70
Ethanol C_2H_5OH	L	—276.98	—174.14	160.67
Ethanol C_2H_5OH	G	—234.81	—168.28	282.59
Acetic acid CH_3COOH	L	—484.09	—389.36	159.83

Appendix IX

Specific Heats of Liquids and Aqueous Solutions of Various Compounds (kJ/kg K)

Substance	Temperature, °C							
	−20	0	20	40	60	80	100	120
Nitric acid,								
100%	1.738	1.750	1.759	1.779	1.8	1.821	1.842	1.863
50%	—	2.793	2.847	2.902	2.973	3.057	3.098	3.182
Ammonia (liquid)	4.522	4.606	4.731	4.857	5.108	6.443	5.736	6.197
Ammonia water,								
25%	—	4.313	4.313	4.354	4.438	4.522	4.606	4.731
Aniline	—	1.997	2.039	2.085	2.127	2.173	2.215	2.261
Acetone	2.052	2.114	2.177	2.24	2.303	2.37	2.445	2.244
Benzene	—	1.633	1.729	1.826	1.926	2.022	2.119	2.177
Water	—	4.229	4.183	4.179	4.606	4.187	4.229	4.271
Glycerol, 50%	—	3.559	3.559	3.517	3.517	—	—	—
Sulphur dioxide								
(liquid)	1.311	1.327	1.369	1.432	1.52	1.629	1.759	1.913
Dichloroethane	0.971	1.057	1.147	1.03	1.327	1.419	1.512	1.599
Diethyl ether	2.16	2.211	2.2665	2.408	2.65	2.889	3.128	3.634
Calcium chloride,								
25%	2.818	2.889	2.939	2.973	3.057	3.098	3.14	3.182
Methanol								
100%	2.382	2.466	2.567	2.667	2.763	2.864	2.964	3.065
40%	—	3.517	3.559	3.601	3.601	3.643	3.685	3.726
Sodium hydroxide								
50%	—	—	3.237	3.22	3.211	3.203	3.195	3.19
30%	—	3.45	3.517	3.584	3.622	3.639	3.22	3.639
10%	—	3.693	3.768	3.819	3.844	3.86	3.869	3.877
Sodium chloride,								
20%	—	3.94	3.932	3.919	3.898	3.894	3.852	3.852
Oleum, 20%	—	1.365	1.424	1.482	1.541	1.599	1.658	1.717
H_2SO_4								
98%	—	1.403	1.457	1.532	1.57	1.625	1.683	1.733
75%	1.805	1.872	1.939	2.006	2.073	2.345	2.207	2.274
60%	2.114	2.198	2.282	2.366	2.449	2.533	2.617	2.703
HCl	—	2.303	2.47	2.638	2.805	3.015	3.182	3.35
Toluene	1.52	1.612	1.704	1.796	1.888	1.98	2.068	2.119
CH_3COOH								
100%	—	1.884	1.826	2.102	2.207	2.315	2.424	2.533
50%	—	3.057	3.098	3.14	3.182	3.266	3.308	3.35

Appendix IX (cont.)

Substance	Temperature, °C							
	−20	0	20	40	60	80	100	120
Phenol (melt)	—	—	2.345	2.345	2.345	2.345	2.345	2.345
Chlorobenzene	1.193	1.256	1.319	1.382	1.445	1.507	1.574	1.637
Carbon tetrachloride	0.812	0.837	0.863	0.892	0.921	0.946	0.976	1.005
Ethyl acetate	1.775	1.846	1.918	1.989	2.064	2.135	2.207	2.278
Ethanol								
100%	2.114	2.29	2.483	2.713	2.964	3.22	3.513	3.806
40%	—	3.433	3.517	3.643	3.685	3.81	3.936	3.936

Appendix X

The Specific Heat c (kJ/kg K), Viscosity μ (kPa s), and Heat Conductivity λ (W/m K) of Various Gases and Vapours

Substance	Temperature, °C								
	−0	100	200	300	400	500	600	700	800
Nitrogen									
c	1.038	1.043	1.050	1.068	1.093	1.114	1.139	1.159	1.187
μ	0.0166	0.0208	0.0246	0.028	0.0311	0.0339	0.0366	0.039	0.0413
λ	0.024	0.031	0.038	0.045	0.051	0.056	0.062	0.064	0.0672
Ammonia									
c	2.05	2.207	2.391	2.575	2.738	2.935	3.098	3.258	3.4
μ	0.0091	0.0128	0.0165	0.0199	0.0234	0.0264	0.0243	0.0321	0.0348
λ	0.021	0.030	0.037	0.044	0.052	0.058	0.064	0.070	0.076
Acetylene									
c	1.633	1.8809	2.073	2.211	2.744	2.420	2.506	2.5455	2.655
μ	0.0096	0.0127	0.0154	0.0176	0.0202	0.0223	0.0243	0.0261	0.0278
λ	0.017	0.023	0.028	0.032	0.036	0.04	0.044	0.047	0.05
Acetone									
c	1.256	1.537	1.788	2.441	2.236	2.428	2.588	—	—
μ	0.0069	0.0094	0.0128	0.0147	0.0174	0.0200	0.0228	—	—
λ	0.0097	0.0172	0.027	0.039	0.052	0.067	0.084	—	—
Benzene									
c	0.94	1.336	1.675	1.955	2.181	2.349	2.525	—	—
μ	0.007	0.0092	0.0121	0.146	0.0172	0.0198	0.0223	—	—
λ	0.0092	0.0172	0.028	0.042	0.057	0.076	0.096	—	—

Appendix X (cont.)

Substance	Temperature, °C								
	−0	100	200	300	400	500	600	700	800
Hydrogen									
c	14.194	14.445	14.487	14.529	14.571	14.654	14.780	14.848	15.115
μ	0.0084	0.0103	0.0121	0.0139	0.0154	0.0169	0.0183	0.0197	0.0210
λ	0.174	0.216	0.258	0.300	0.341	0.383	0.425	0.466	0.588
Steam									
c	1.859	1.893	1.964	2.001	2.064	2.207	2.213	2.274	2.345
μ	0.0085	0.0023	0.0166	0.0198	0.0232	0.0266	0.0299	0.0331	0.0361
λ	0.016	0.024	0.033	0.043	0.055	0.068	0.082	0.098	0.115
Air									
c	1.005	1.01	1.025	1.047	1.068	1.093	1.114	1.135	1.156
μ	0.0171	0.0218	0.0259	0.0294	0.0320	0.0357	0.0384	0.0411	0.0437
λ	0.024	0.032	0.039	0.046	0.052	0.057	0.022	0.066	0.070
Sulphur dioxide									
c	0.607	0.662	0.712	0.754	0.783	0.808	0.825	0.837	0.850
μ	0.0121	0.0161	0.020	0.0238	0.0275	0.0313	0.035	0.0356	0.0421
λ	0.008	0.012	0.017	0.02	0.026	0.031	0.036	0.042	0.046
Carbon dioxide									
c	0.816	0.913	0.992	0.055	1.110	1.143	1.193	1.223	1.218
μ	0.0138	0.0184	0.0226	0.0264	0.0299	0.0332	0.0362	0.0381	0.0418
λ	0.015	0.023	0.031	0.039	0.047	0.055	0.062	0.069	0.075
Diethyl ether									
c	1.44	1.842	2.223	2.588	2.943	3.274	3.609	—	—
μ	0.0069	0.0093	0.0117	0.014	0.0165	0.0188	0.0212	—	—
λ	0.013	0.023	0.035	0.05	0.067	0.086	0.108	—	—
Oxygen									
c	0.917	0.934	0.963	0.997	1.026	1.047	1.063	1.0844	1.101
μ	0.0192	0.0244	0.0290	0.0331	0.0369	0.0403	0.0435	0.0465	0.0493
λ	0.025	0.0388	0.04	0.048	0.055	0.061	0.067	0.073	0.077
Methane									
c	2.165	2.449	2.805	3.174	3.530	3.856	4.154	4.438	4.648
μ	0.0104	0.0133	0.0161	0.0185	0.0208	0.0227	0.0246	0.0265	0.0282
λ	0.030	0.041	0.052	0.062	0.072	0.024	0.091	0.093	0.051
Nitric oxide									
c	0.95	0.978	1.009	1.034	1.055	1.08	1.097	1.114	1.135
μ	0.018	0.0229	0.0268	0.0306	0.034	0.037	0.04	0.0428	0.0453
λ	0.021	0.027	0.033	0.038	0.043	0.048	0.052	0.055	0.060

Appendix X (cont.)

Substance	Temperature, °C								
	−0	100	200	300	400	500	600	700	800
Carbon monoxide									
c	1.038	1.047	1.059	1.08	1.105	1.130	1.156	1.181	1.193
μ^1	0.0166	0.0209	0.0246	0.0278	0.0309	0.0338	0.0366	0.0387	0.041
λ	0.023	0.030	0.036	0.042	0.048	0.054	0.060	0.0665	0.070
Toluene									
c	1.03	1.411	1.75	2.047	2.294	2.504	2.671	—	—
μ	0.0066	0.0089	0.011	0.0132	0.0154	0.0175	0.0196	—	—
Chlorine									
c	0.858	0.988	1.013	1.030	1.038	1.04	1.055	1.059	1.063
μ	0.0122	0.0168	0.021	0.0254	0.0287	0.0322	0.0356	0.0367	0.0416
λ	0.007	0.010	0.012	0.015	0.017	0.019	0.021	0.23	0.025
Hydrogen chloride									
c	0.800	0.800	0.804	0.808	0.821	0.833	0.850	0.867	0.879
λ	0.0132	0.0182	0.0229	0.0277	0.0313	0.0353	0.0388	0.0423	0.0456
Ethylene									
c	1.407	1.738	2.064	2.395	2.729	3.027	3.383	3.710	4.04
μ	0.0096	0.0127	0.0156	0.0182	0.0206	0.0228	0.0249	0.0266	0.0387
λ	0.016	0.029	0.0441	0.059	0.064	0.092	0.108	0.123	0.135
Ethanol									
c	1.340	1.687	2.01	2.32	2.613	2.893	3.166	—	—
μ	0.0079	0.0108	0.0137	0.0167	0.0197	0.0226	0.0257	—	—
λ	0.013	0.023	0.03	0.05	0.067	0.085	0.107	—	—

Appendix XI

Solubilities of Some Gases in Water at Various Temperatures

Gas	Amount of gas (cm^3) dissolved in 1 dm^3 of water			
	0 °C	20 °C	40 °C	60 °C
Nitrogen	23.6	16.0	12.5	10.2
Acetylene	1 730	1 030	—	—
Ammonia	1 300 000	710 000	—	—
Hydrogen	21.5	18.4	16.4	16.0
Air	28.8	18.7	14.2	12.2

Appendix XI (concl.)

Gas	Amount of gas (cm^3) dissolved in 1 dm^3 of water			
	0 °C	20 °C	40 °C	60 °C
Sulphur dioxide	800	395	190	—
Carbon dioxide	1 713	878	530	360
Oxygen	49	31	23	19
Methane	55.6	31.1	23.7	19.5
Carbon monoxide	35.4	23.2	17.8	14.9
Hydrogen sulphide	4 670	2 580	1 660	1 190
Chlorine	—	2 260	1 485	—
Hydrogen chloride	507 000	442 000	386 000	339 000
Ethylene	226	122	—	—

Appendix XII

The Mean Head Coefficients ε for the Froth Apparatus Grate

Gas velocity, m/s	Intensity of liquid flow, m^3/m^2 h									
	1.0	2.0	3.0	4.0	5.0	7.5	10.0	12.5	15.0	20.0
1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
1.5	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
2.5	1.10	1.12	1.14	1.16	1.18	1.22	1.25	1.30	1.35	1.40
3.0	1.80	1.85	1.90	1.95	2.00	2.10	2.25	2.40	3.0	—
3.5	2.70	2.80	2.85	2.95	3.00	3.20	3.40	—	—	—

The Mean Values of the Coefficient ψ

Gas velocity, m/s	Intensity of liquid flow, m^3/m^2 h								
	1.0	2.0	3.0	4.0	5.0	7.5	10.0	12.5	15.0
1.0	0.50	0.62	0.71	0.80	0.85	0.88	0.90	0.95	1.0
1.5	0.46	0.57	0.65	0.76	0.81	0.84	0.88	0.95	1.0
2.0	0.44	0.53	0.61	0.71	0.77	0.82	0.85	0.95	1.0
2.5	0.42	0.50	0.58	0.68	0.75	0.80	0.84	0.95	—
3.0	0.58	0.63	0.68	0.76	0·81	0.90	1.00	1.00	—
3.5	0.65	0.69	0.73	0.78	0.83	0.93	—	—	—
Mean	0.50	0.60	0.65	0.75	0.80	0.85	0.90	0.95	1.0

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